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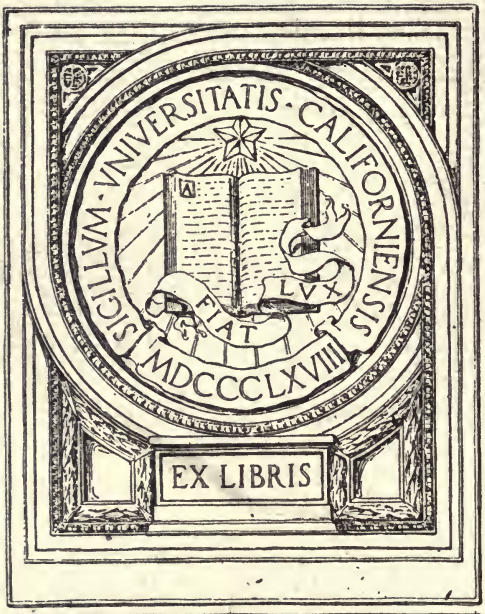
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FOR THE

ENAMEL INDUSTRY

AND

THEIR CHEMICAL TECHNOLOGY.

BY

JULIUS GRÜNWALD, DR.ING.,

OFFICIER D'ACADÉMIE; TECHNICAL CHEMIST AND CONSULTING ENGINEER, VIENNA;
FORMERLY WORKS MANAGER, LAFESCHOTTE (DOUBS).

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TRANSLATED BY

HERBERT H. HODGSON,

M.A. (CAMB)., B.SC. (LOND.), PH.D. (HEIDELBERG),

FORMERLY MAJOR SCHOLAR OF TRINITY COLLEGE, CAMBRIDGE, AND BRADFORD CITY TRAVELLING SCHOLAR; LATE LECTURER AND RESEARCH CHEMIST AT THE BRADFORD TECHNICAL COLLEGE; HEAD OF THE CHEMICAL DEPT. AT THE NORTHERN POLYTECHNIC INSTITUTE, LONDON.

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TRANSLATOR'S PREFACE.

THE very hearty reception accorded to his previous books—*The Theory and Practice of Enamelling on Iron and Steel* and *The Technology of Iron Enamelling and Tinning**—both in this country and in America, has led Dr. Grünwald to submit the present volume with the intention of solving many difficulties connected with Raw Materials which could not be dealt with in the above-named works.

This volume appears at a psychological moment in the history of nations, when dependence upon our own resources has never been so emphasized, and deals with an industry which has developed entirely within the last twenty years, and is now of profound economic significance. When one considers that something approaching 50,000 persons find their livelihood as enamellers in German speaking countries, and that a large part of their output finds a market in England, it will be realised that the cutting off of supplies will cause a gap in kitchen economics not easy to fill. Consequently, a very lucrative industry waits the enterprise of English manufacturers.

The series of three books written by Dr. Grünwald, who is one of the foremost experts in enamelling technology, will serve as a valuable source of information for commencing operations, and there is no reason whatever why British capital should not enter this field, since the raw materials are cheap and abundant, their chemistry is comparatively simple, and our iron trade can supply the requisite vessels for enamelling purposes.

Enamelling is but one of a series of industries which render more efficient our exclusively internal arrangements, and it is

* Published by Charles Griffin & Co., Ltd., London.

almost a truism to state that whenever possible such should always find their seat at home and not in foreign lands.

It is, therefore, the hope of the publishers and of the translator that these valuable treatises on enamelling technology should not only prove of service to those already engaged in the trade, but should serve as an impetus to industrial development.

H. H. H.

Northern Polytechnic Institute,
August, 1914.

PREFACE.

THE enamel manufacture is one of the youngest branches of the ceramic industry, and comprises the wholesale production of enamelled utensils made of cast and sheet iron. It is, therefore, of interest as a connecting link between the ceramic and iron trades.

Although enamel in its origin dates back to grey antiquity, while later it has served for the production of valuable artistic wares, nevertheless the technique of enamelling iron objects is comparatively modern.

During the last fifteen years in particular, this industry has become of extraordinary economic significance, and to-day employs 25,000 persons in Germany alone, while in Austria-Hungary 17,000 to 19,000 people are engaged. The annual German output is estimated at 90,000,000 kilos.

This almost unexampled industrial development is intimately connected with the period when old empirical methods were abandoned, and the operations superintended by scientifically trained men.

The technical literature dealing with the subject is as yet somewhat meagre, and although in recent years gratifying progress has to be recorded, nevertheless many problems concerning enamel manufacture still await solution.

On the assumption that for exact knowledge of a work's procedure an acquaintance with the chemical and mineralogical technology of the raw materials, now used in such enormous quantities, is indispensable, the author has endeavoured in this volume to give the latest practice and research in as compressed and popular manner as possible. Interesting material has been collected from scattered sources and supplemented by the author's personal experience.

Every man engaged in practice realises the desire for more extensive knowledge, and is aware of the ignorance existing in certain circles of non-chemically trained enamel managers as to observed facts and their explanation. The author will be happy if by this book he renders the industry a service, and trusts it will meet with the same reception in interested quarters as experienced by his previous treatise on the *Theory and Practice of Enamelling on Iron and Steel.**

Since almost all the raw materials for enamelling purposes also find analogous employment in purely ceramic industries, the book may find a special interest there as a work of reference.

I, therefore, submit my effort to the indulgent criticism of my industrial associates with the wish that it may prove of value to them.

DR. JULIUS GRÜNWALD.

VIENNA, 1913.

* Published by Charles Griffin & Co., Ltd., London.

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UNIV. OF CALIFORNIA

RAW MATERIALS

FOR THE

ENAMEL INDUSTRY.

I. FELSPAR.

THE felspars constitute a special group of the silicates, the individual members being classified mineralogically as follows :—

I. Monoclinic, orthoclase, or potash felspar, of chemical formula $K_2Al_2Si_6O_{16}$.

II. Triclinic felspars, further subdivided into

(1) Microcline, chemically identical with orthoclase.

(2) Plagioclase, having the varieties :—

(*a*) Albite or soda felspar of chemical formula $Na_2Al_2Si_6O_{16}$. Orthoclase, microcline, and albite are, therefore, alkali felspars (viz., potash or soda).

(*b*) Anorthite, also termed lime felspar, $CaAl_2Si_2O_8$. Albite and anorthite are isomorphous—*i.e.*, they possess the same crystalline form, but differ in chemical composition. In addition, there are lime-soda felspars, which for our purpose, however, are of subordinate importance.

Orthoclase crystallises in the monoclinic system (possessing three unequal crystallographic axes, two of which are obliquely inclined, and the third perpendicular to their plane). Orthoclase exhibits a tendency to form twin crystals. The crystals occur either singly or drusy, possess cleavage in two directions, and exhibit either a flesh-coloured, pure white (often yellowish), reddish (due to traces of iron oxide), or light grey coloured fracture. The hardness is 6,* and the specific gravity varies from 2·54 to 2·58.

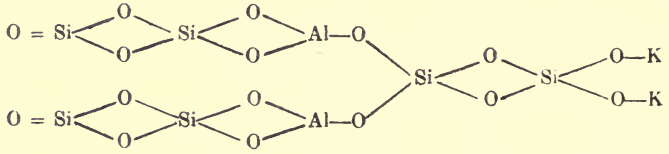
* See Scale of Hardness at end of book.

The chemical composition corresponds to the formula :—

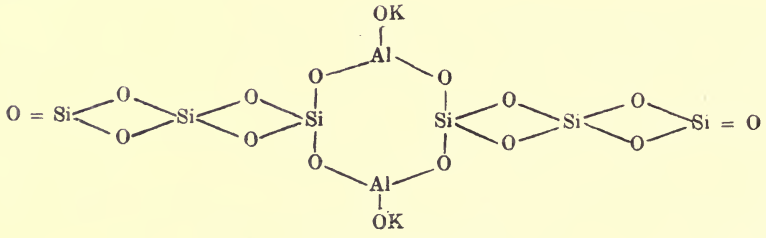
$$K_2Al_2Si_6O_{16} = K_2O + Al_2O_3 + 6SiO_2,$$

possessing 64·72 per cent. silica (SiO_2)
18·35 per cent. alumina (Al_2O_3)
16·93 per cent. potassium oxide (K_2O).

As a rule, orthoclase contains 2 to 3 per cent. sodium oxide (Na_2O), and sometimes even as much as 8 per cent. The frequent presence of traces of lime (CaO), magnesia (MgO), iron oxide (Fe_2O_3), and water (H_2O), depends on foreign inclusions or impurities introduced by neighbouring minerals. Traces of barium are of more seldom occurrence (barium felspar—Celsian). Orthoclase fuses with difficulty in the blowpipe to a milky-white opaque glass, and its melting point lies a little beyond 1,200° C. It is only feebly attacked by hot hydrochloric acid (HCl), although readily decomposed by hydrofluoric acid (HF). In a finely divided condition orthoclase gives a definite alkaline reaction when triturated with water. Orthoclase occurs as an important constituent of many of the older volcanic rocks at Carlsbad, Elbogen, Petschau in Bohemia, Bischofsgrün in the Fichtelgebirge, Hirschberg and Striegau in Silesia, Baveno on Lake Maggiore, Valfloriani at Fleims, the Isle of Elba, Arendal, and in the Urals, etc. According to Tschermak,* the graphic formula of orthoclase is :—



Glinka also has proposed the following interesting structural formula for orthoclase :—



* *Mineral-Mittlg.*, 1871, section 2.

Microcline.—This is a potash felspar chemically identical with orthoclase. The crystals themselves are frequently found as extremely fine, regular, lamellæ.

Plagioclase.—To the special group of plagioclase felspars belong :—

(1) Albite, sometimes termed soda felspar, which is a soda-alumino-silicate, $Na_2Al_2Si_6O_{16}$.

(2) Anorthite, or lime felspar, $Ca_2Al_4Si_4O_{16}$.

(3) Lime-soda and soda-lime felspars.

Tschermak shows that only albite and anorthite are to be regarded as individuals, the other triclinic felspars containing sodium and calcium being regarded as isomorphous mixtures of 1 and 2 in varying proportions.

The triclinic system is characterised by three unequal, obliquely inclined, crystallographic axes.

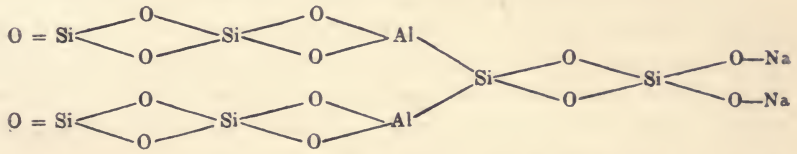
Albite.—This triclinic plagioclase or soda felspar possesses only subordinate interest for the enamel manufacturer. As a rule it crystallises in twins. Ordinary white albite or pericline is found in massive, granular, laminated, and striated aggregates. It shows cleavage, the faces being streaked. The hardness varies from 6 to 6·5, and the specific gravity 2·61 to 2·64. The colour may be white, light red, yellow, green, and even brown. It exhibits a vitreous lustre, sometimes has a blue opalescence, and may be transparent to translucent. Albite colours the flame a clear yellow (in consequence of its high sodium content), and exhibits alkaline properties.

The chemical composition of pure albite is :—

$$Na_2Al_2Si_6O_{16} = Na_2O + Al_2O_3 + 6SiO_2,$$

containing
68·84 per cent. SiO_2
19·40 per cent. Al_2O_3
11·97 per cent. Na_2O.

The graphic representation of albite is as follows :—



In most specimens lime is present (on an average 2 per cent. CaO) from included anorthite (lime felspar) together with a little

potash. Albite is never found chemically pure. Pericline, which is of special interest to us, is a soda-lime felspar found in Alpine cavities.

Localities for albite are the chlorite schists of Penig and Siebenlehn in Saxony, Hirschberg in Silesia, Zöptau in Moravia, St. Gothard, Thus, Piz Valatsch on Mt. Skopi, Weidalpe in the Salzburg, Habachtal, Pfunders in the Alps, Elba, and in enormous masses in Norway and Sweden.

Anorthite.—This variety of plagioclase is a triclinic lime felspar, but of no importance for enamelling purposes. Its chemical formula is :—

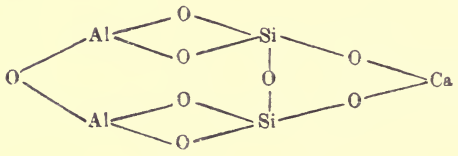
$$Ca_2Al_4Si_4O_{16} = 2CaO + 2Al_2O_3 + 4SiO_2,$$

and contains

43·28 per cent. SiO_2,
36·62 per cent. Al_2O_3,
20·10 per cent. CaO.

It is found in Corsica, Gabbro near Harzburg, Neurode in Silesia, Hammerfest and Radmansö in Sweden, Yamosk in Canada, in the andesite of the Aranger Mountains in Siebenburgen, and Commontry in France.

Anorthite is the most basic of all felspars possessing the following graphic formula :—



LIME-SODA AND SODA-LIME FELSPAR OR OLIGOCLASE.

This triclinic felspar, made up of albite and anorthite, plays no part in enamelling. The hardness and specific gravity are similar to the previous felspars, while the colour is grey or yellowish-white. Since it contains a silica content varying from 62 to 65 per cent., it is more easily fused than orthoclase and less readily than albite, being feebly attacked by acids, although these are more potent the greater the lime content.

These felspars are extensive constituents of rock masses, mainly consisting of quartz and orthoclase, especially gneiss.

The localities are Arendal and Tvedestrand in Norway, Pargas and Kimito in Finland.

General Information on the Felspars as Enamel Constituents.—It is of the highest importance to know the content of silica, alkali, and alumina of any felspar used for enamel preparations. In round numbers a good potash felspar should possess the following composition :—

65 per cent. SiO_2,
18 per cent. Al_2O_3,
16·5 per cent. K_2O.

Soda felspars are seldom used for enamels, although frequently a small part of the potassium in the potash felspar has been replaced by sodium. When soda felspars are employed in place of potash varieties, care must be exercised that equivalent amounts are taken to preserve the same relationship at melting, since about 40 sodium oxide exerts the same influence as 60 potassium oxide. The greater or less content of such impurities as iron oxide (Fe_2O_3), magnesia (MgO), and lime (CaO), which are generally present, have an obvious effect upon the readier fusibility of the spar.

The iron oxide content must not exceed certain narrow limits (at the most 0·6 per cent.), since discolouration (a reddish-yellow tint) can occur in the case of white enamels, and, therefore, spars of deep red appearance are excluded. A grey to yellow aspect, however, which is chiefly due to organic impurity, is not deleterious, although even in this case a roasting test may be made with advantage, since most spars tinted in this way appear white after firing.

On the other hand, appreciable amounts of quartz, mica, clay, and similar minerals, are injurious. The spars from Bergen in Norway often exhibit almost every possible shade from fleshy-red, grey, blue, apple-green to white ; those from Arendal (Norway) are a dark smoky grey, while the spars from Bischofsteinitz in Bohemia are a pure white. All these shades disappear on roasting or when fused in the enamel, leaving behind a pure milky-white appearance.

Amorphous felspars, or rocks containing felspars, which do not exhibit lustrous cleavage faces, are to be excluded from use.

The following table gives some typical analyses of felspars and pegmatites :—

	Felspars.								Pegmatite.				
	Norway.	Norwegian Albite.	Norwegian Orthoclase.	Bischofsteinitz.	Halle.	Fichtelgebirge.	Quabenstein (Bay).	Chanteloupe (France).	Chinastone (Cornwall).	St. Yrieux.	Regensburg.	Limoges.	St. Austell.
Silica, SiO_2,	64·44	66·27	66·59	63·11	62·76	70·10	61·37	64·00	74·34	74·3	87·78	74·38	74·91
Alumina, Al_2O_3,	18·75	18·92	18·25	19·76	19·20	17·16	20·23	20·56	18·40	18·3	7·36	15·21	16·04
Lime and Magnesia, $CaO + MgO$,	0·27	0·73	0·91	2·27	0·64	1·43	0·55	0·38	0·24	0·6	0·29	1·38	1·44
Potassium oxide, K_2O,	13·82	1·34	12·43	14·57	14·90	1·52	15·75	14·99	6·00	6·5	1·60	3·96	3·06
Sodium oxide, Na_2O,	2·40	11·67	1·08	..	..	8·65	..	..	..	..	1·00	4·85	3·45
Iron oxide, Fe_2O_3,	0·65	1·14	0·58	0·45	..	0·91	0·45	..	..	..	0·84	0·56	0·55
Water + loss on heating,	..	..	..	..	1·70	..	1·31	..	0·96	0·3	1·34	0·42	0·54

AMERICAN FELSPARS.

	Canadian Potash Felspar. Brand T.	Connecticut Potash Felspar. Brand U.	Maryland Soda Felspar. Brand V.
	Per cent.	Per cent.	Per cent.
Potassium oxide, K_2O, . . .	13·70	9·46	0·20
Sodium oxide, Na_2O, . . .	2·02	4·21	8·03
Lime, CaO, ...	0·23	0·16	0·49
Magnesia, MgO, ...	0·10	0·30	2·46
Alumina, Al_2O_3, ...	19·20	16·43	22·11
Ferric oxide, Fe_2O_3, ...	0·23	0·63	0·62
Silica, SiO_2, ...	64·30	68·79	66·08

Pegmatite, which is a rock made up of felspar and quartz, cannot be recommended for enamels, but if so used the quartz content of the enamel must be correspondingly diminished, or a smaller quantity of felspar taken, and the sodium deficiency made up by means of ordinary soda.

For example, 100 kg. pegmatite with 74·3 per cent. SiO_2 and 6 per cent. alkali corresponds to about 114 kg. potash felspar (65 per cent. SiO_2), and the latter contains about 6·9 kg. K_2O. Since 100 kg. pegmatite only contains 6 per cent. K_2O, therefore 2 per cent. K_2O must be added in the form of potash (1 kg. potash = 0·68 kg. K_2O, and, therefore, 2·9 kg. potash contains 2 kg. K_2O). England annually exports over 35,000 tons of pegmatite.

The interesting problem of the formation of clay or kaolin from felspar, which is so very important from the enameller's standpoint, will be more fully dealt with in the chapter on Clay. At this stage only a selection will be made from the investigations on the relatively easy decomposition of felspar by carbonic acid, and even by water alone, to show how readily alkali may be partially abstracted from felspar thereby, as also by prolonged wet grinding.

It is a noteworthy fact * that certain natural silicates are easily decomposed by acids, but that others exhibit a contrary behaviour—*e.g.*, glass, which contains the same bases united to silica as the majority of rocks, although in a certain state of equilibrium, is decomposed much more rapidly by water than by acids. It appears as though many rock-forming minerals have a similar behaviour. To throw light upon the kaolinisation of felspars, laboratory experiments have been conducted in the following way :—A finely powdered felspar (passed through a 200-mesh sieve) was stirred with distilled water to a thin paste and placed in an unglazed porous pot containing an ordinary

* *Trans. Amer. Ceram. Soc.*, vol. viii., 1906; also *Chem. Ztg.*, 1907, vol. xiii., p. 581.

arc-lamp carbon electrode, the pot being then put into a large glass cylinder filled with distilled water. The second carbon electrode is introduced between the porous cell and the glass wall, and a current of about 110 volts established, the inner electrode being connected to the positive pole. With about 200 grammes felspar the current strength seldom exceeds 0·05 ampère. By the current passage, water is attacked at the anode —*i.e.*, inside the porous pot—whereas externally the cathode water is enriched with alkali at the expense of the potassium in the orthoclase. The reaction, however, is not of lengthy duration. When the felspar is powdered dry not more than 0·03 per cent. alkali could be abstracted, but when ground wet the disintegrating action of the water increases, and the alkali loss amounts to between 0·3 and 0·4 per cent. In later experiments this method was somewhat modified ; orthoclase, ground at the mill, was electrolysed until the alkali given off became quite inappreciable, when the paste was removed, reground for several hours, and again submitted to electrolysis. By employing a felspar containing 11·4 per cent. alkali it was possible to extract 3·6 per cent. alkali, or about one-third of the total content, and this after fourteen repetitions of the above procedure. By continuing this process the complete kaolinisation of the felspar may be accomplished.

The author of this publication draws the following conclusions :—

(1) If felspar be ground with water, decomposition immediately begins, and may be easily detected by adding a few drops of phenolphthalein (test for alkali).

(2) This decomposition does not proceed far, since not more than 0·3 per cent. of alkali can be detected.

(3) By electrolysis up to 0·4 per cent. of alkali may be removed.

(4) As soon as 0·4 per cent. of alkali is dissolved out, the process slackens, without complete cessation, however.

(5) By renewed grinding and electrolysis it was possible to remove 4 per cent. of the original 11 per cent. of soluble bases.

(6) There seems to be no reason why the process cannot be continued until complete transformation of the felspar into kaolin has taken place. Recently this theme has again received attention by Funk,* who, in an extremely suggestive way, found that

* Dr. W. Funk-Meifzen, "Krit. Studien über die Zersetzung des Felspates," *Sprechsaal*, 1910, Nos. 2 and 3.

after twelve hours' wet grinding the felspar lost 0·4 per cent. of the total alkali present, which exceeds Cushmann's result (viz., only 0·03 per cent., see above). According to Doubrée,* 2·8 per cent. of the alkali present is extracted by water after 192 hours' grinding. If very finely powdered felspar be dropped into water, the finest particles only settle slowly, and after some months the uppermost liquid layers appear to be a yellowish-brown solution, which gradually becomes brighter, finally changing to an opalescent colloidal solution capable of passing unchanged through the densest of filters. In this solution 0·1 to 0·2 per cent. of the total alkali present may be established by titration.

Fused felspar is attacked more rapidly by the prolonged action of water, carbonic acid, or both together, than the natural raw material. By water and carbonic acid 1·1 per cent. alkali was dissolved.

Silica and alumina ($SiO_2 + Al_2O_3$) are only extracted to a very minute extent after 192 hours' wet grinding—*e.g.*, Doubrée gives 0·002 per cent. SiO_2 and 0·003 per cent. Al_2O_3. In all the experiments distilled water free from carbonic acid was employed.

Cushmann has urged that all the alkali capable of extraction from the felspar is not really in solution.

The following table gives a summary of the total alkali extracted after fourteen grindings :—

Ground Orthoclase.	Duration of Grinding. In Hours.	Total Alkali Extracted, Calculated in per cent. K_2O.	
		Test No. 1,242.	Test No. 1,300.
Ground sample, sieved through 200-meshed sieve, ...	..	0·15	0·14
Ground dry, ...	2	0·19	0·22
Ground wet, ...	2	0·41	0·15
,, ...	2	0·13	0·14
,, ...	6½	0·23	0·26
,, ...	6½	0·19	0·21
,, ...	6½	0·16	0·17
,, ...	6½	0·18	0·25
,, ...	2	0·12	0·15
,, ...	12	0·45	0·35
,, ...	24	0·46	0·41
,, ...	12	0·43	0·27
,, ...	24	0·39	0·45
,, ...	24	0·40	0·40
,, ...	..	3·89	3·57

* Bischof, *Die feuerfesten Tone*, p. 15.

Felspar in the Enamel Manufacture.—The following numbers afford some notion of the considerable quantities of felspar used in the ceramic industry :—

Germany's import of felspar during 1908 amounted to 42,491,600 kg., of which 19,667,000 kg. came from Norway —*i.e.*, almost half the total—4,272,900 kg. from Austria-Hungary, and 18,130,500 kg. from Sweden.

Concerning the export of Norwegian felspar to Germany, the Norwegian Consul-General in Berlin reported as follows to his Government :—

The felspar requirements of the German porcelain industry have now begun to increase after a lengthy period of depression, although since the German importer has still large consignments unsold from previous years, the prices have not yet advanced; the cheap supply of Norwegian spar, which is delivered in fairly large quantities to Germany, has depressed the price level. The importers are barely able to pay more than 24s. to 24s. 6d. per ton at Stettin for first-class ware. In addition, the northern export has had to compete with material recently found in considerable quantities in Germany itself, particularly in Bavaria and Bohemia, this not only being of fairly good quality, but has the advantage of being close to the centres of the ceramic industry in Upper Francenia, Saxony, and Thuringia.

The majority of German porcelain firms grind their own felspar, since it is desirable to examine the material in the crude condition. For ground felspar, 12s. to 15s. more is paid than for the raw material.

Germany's total felspar import amounted to 42,492 tons in 1908, and 41,369 tons in 1909, valued at 1,487,000 to 1,488,000 shillings. This came from :—

	1909.	1908.
Norway, . . .	20,476 tons.	19,667 tons.
Austria-Hungary, .	4,877 ,,	4,273 ,,
Sweden, . . .	15,811 ,,	18,131 ,,

Germany's felspar export amounted to 9,420 tons in 1908, 10,682 tons in 1909, and went chiefly to Austria-Hungary.

In 1908, Austria-Hungary imported about 8,147,100 kg. of felspar and exported 4,303,200 kg.

Felspar is the main ingredient in enamels by supplying the silica and silicates, while on account of its considerable content

of flux—viz., the alkali and alumina—it exerts a favourable influence on the opacity of the enamels.

Although felspar only fuses above 1,200° C., this temperature is continually exceeded in the Siemens' tank furnace ; the fused felspar exhibits a milky-white aspect.

The bulk of the 40 to 50 per cent. silica which ordinary enamels contain is furnished by the felspar, whether quartz be used in the mixture or not. In the majority of enamel recipes the silica employed is provided, not only by felspar, but also by cheap quartz (together with the relatively small amounts from the clay added on grinding). In the short table below the approximate proportions of felspar and quartz are given, such as are present in first-class enamel recipes :—

Examples of the Ordinary Proportions possible between Felspar and Quartz. Percentage Ratio of Felspar to Quartz in the Raw Mixture.

Ground.	Common White.	Soft White.	Acid-free White.	White for Cast.	Powder White.	Blue.
25 : 21	15 : 30	25 : 9	6 : 47	39 : 0	26 : 0	29 : 18
26 : 18	26 : 19	..	13 : 36	31 : 19	..	34 : 20
28 : 16	20 : 28	..	17 : 40	26 : 13	..	38 : 23
31 : 21	27 : 14	..	..	42 : 0	..	44 : 0
40 : 1	30 : 8	..	..	46 : 0	..	57 : 8
40 : 3	34 : 19	..	..	..	..	..
..	39 : 0	..	..	..	..	..

These proportions have obviously no limiting values, but are merely the customary quantities for current trustworthy enamels.

If the silica content of the pure quartz used be taken at 100, and that of a good quality felspar at about 65, then the quartz equivalent of the felspar is such that 100 kg. felspar = 65 kg. quartz, or 100 kg. quartz = 154 kg. felspar. This is naturally apart from the alumina and alkali content of the felspar, which themselves have to be correspondingly supplemented by alkali (soda, potash, etc.), and clay (alumina and silica) to acquire the average composition necessary.

The following is an example of such a calculation :—

Taking the theoretical case of an enamel recipe, in which the initial mixture should contain 30 kg. felspar and 8 kg. quartz, but the felspar is omitted and has to be replaced by quartz,

the problem is to find how much quartz, clay, and alkali have to be taken in the new recipe.

From the above data, 30 kg. felspar correspond to

$$\frac{64{\cdot}4 \times 30}{100} = 19{\cdot}32 \text{ kg. quartz.}$$

Also, 30 kg. felspar contain

$$\frac{18{\cdot}8 \times 30}{100} = 5{\cdot}64 \text{ kg. } Al_2O_3,$$

$$\frac{13{\cdot}82 \times 30}{100} = 4{\cdot}15 \text{ kg. } K_2O,$$

and

$$\frac{2{\cdot}40 \times 30}{100} = 0{\cdot}72 \text{ kg. } Na_2O.$$

The alumina (Al_2O_3) is replaced by the corresponding amount of clay. Now, 100 kg. clay has the composition (see *Clay*)—

46·6 per cent. SiO_2,
38·7 per cent. Al_2O_3,
14·3 per cent. water, etc.

Therefore, to replace the 5·64 kg. alumina of the felspar, the addition must be made of $\frac{5{\cdot}64 \times 100}{38{\cdot}7} = 14{\cdot}4$ kg. clay. At the same time, however, silica will be introduced into the mixture by the clay; therefore, to avoid excess, the number of kilos. silica contained in the 14·4 kg. clay must be calculated and the quartz content diminished by this amount.

100 kg. clay contain 46·6 kg. silica, and, therefore, 14·4 kg. clay contain 6·71 kg. silica. Accordingly, only 19·32 − 6·71 = 12·61 kg. quartz must be taken.

Finally, there is the replacement of the 4·15 kg. K_2O and 0·72 kg. Na_2O contained in the felspar, either by potash (K_2CO_3) or saltpetre (KNO_3), and by soda (Na_2CO_3) or sodium nitrate ($NaNO_3$) respectively. In most cases potash and soda are chosen.

100 kg. potash contain about 90 per cent. pure K_2CO_3, and, therefore, correspond to 0·682 × 90 = 61·38 kg. K_2O.

Therefore, to replace 4·15 kg. K_2O of the 30 kg. felspar by K_2CO_3, $\frac{4{\cdot}15 \times 100}{61{\cdot}4} = 6{\cdot}75$ kg. potash must be taken.

Also, 100 kg. calcined soda (see *Soda*) corresponds to 58·5 kg.

K_2O, and to replace the 0·72 kg. Na_2O of the 30 kg. felspar by soda, $\frac{0{\cdot}72 \times 100}{58{\cdot}5} = 1{\cdot}2$ kg. must be taken.

Therefore, collecting the data together, it is found that 30 kg. felspar may be replaced in the recipe by

12·61 kg. quartz,
14·40 kg. clay,
6·75 kg. potash,
1·20 kg. soda.

The point must be emphasized, however, that, as a rule, it is inadvisable to replace the felspar silica by quartz or clay, even though the equivalent proportions are observed, without further information. Although chemically there is identity, yet in practice it is known that two enamels of the same chemical constitution exhibit different properties, according to the quality of the raw materials furnishing the silica, alumina, and alkali. The chemical analysis of an enamel may, for example, afford 40 per cent. SiO_2, 19 per cent. alkali, 10 per cent. alumina, etc., and this composition may be arrived at in various ways, such as introducing the silica in the form of quartz and clay, and the alkali as alkaline carbonate or nitrate, or by taking the corresponding amounts of felspar, clay, and carbonates. In both the above cases enamels with identical chemical compositions are obtained, which in practice, however, exhibit considerable divergence in such physical properties as expansion, opacity, fusion point, etc. The author * has dealt with this interesting theme in an earlier publication.

In earlier times felspar was obtained in lumps, which were roasted, splintered by water, and powdered in the enamel works themselves by cylindrical and drum mills.

This process, which is now only of limited application, has much to recommend it, for the expert can judge pretty accurately from the appearance, structure, and colour of a lump of felspar as to its purity and value. Many impurities of an organic character acquired during transport—*i.e.*, from the ship's hold or in the trucks—are burnt during the roasting operation. The trade, however, has gradually adopted the plan of purchasing felspar

* J. Grünwald, *Beitrag zur Chem. Technologie der Email-industrie*, *Oest. Chem. Ztg.*, 1908.

in a finely powdered condition, whereby not only has the merchant benefited (since now felspar fragments formerly rejected are ground up, while an economy in transport wages has been effected), but the enameller as well.

The continuous increase in the production of enamelled wares, the more limited accommodation for storage, furnaces, etc., and, above all, the growing knowledge as to the most important raw materials to use, have had the effect of making the powdered form of felspar preferable.

Naturally the above presumes a conscientious merchant, while the chemical analysis of such a felspar becomes of paramount importance.

Stress must here be laid as to the limits of the silica content. A felspar whose analysis gives a silica content exceeding 66 to 68 per cent. is of inferior quality, and to be rejected. The merchant having become advised as to the silica content may correspondingly reduce his price, and it then becomes the business of the enameller to adapt his enamel formula to the higher silica content of the felspar. This case, however, seldom occurs, and it is the practice to employ felspar of only first-class quality whose composition approaches the ideal standard as closely as possible.

It is also important to establish the ferric oxide content of the felspar, since this in excess will discolour white enamels. For ground or blue enamels a felspar with a moderate excess of iron oxide is not injurious, while the price is much less. The moisture content must also be established, since this may be fairly high, owing to bad storage, and the consequent loss in weight may render valueless a most trustworthy enamel recipe. For example, take a works in which for years an established enamel formula has been employed requiring 30 per cent. felspar, and that the latter accidentally contains 8 per cent. moisture; in this case the felspar content will be deficient by 8 per cent., which is certainly not an advantage.

The iron oxide content, as a rule, should hardly exceed 0·6 to 0·7 per cent. The felspar, as also the other raw materials, should be stored in specially protected cases, which are kept scrupulously clean.

An interesting property of fused felspar may now be mentioned —namely, that it possesses a lower specific gravity than the natural variety. It exerts a condensing influence upon the

enamel melt, which is the more intense, and renders the enamel more opaque, the finer its state of division when added to the mixture.

The alumina content of felspar possesses a covering power not to be under-estimated, and, as a rule, white enamels are most advantageously prepared as purely felspar enamels, to the exclusion of quartz.

II. QUARTZ.

Although felspar furnishes silica in addition to alumina and alkali for the manufacture of enamels, yet the relatively cheaper quartz, which is almost pure silica, finds extensive application.

Since enamels are mainly compounds of silicic acid, quartz often furnishes a part and, in some isolated cases, the whole of the silica necessary for the enamel. Quartz is found extensively in great masses, either in the pure state or as a constituent of various rocks.

When pure, quartz occurs in hexagonal crystals, having usually a pyramidal form. As rock crystal and as pebbles in river beds it often assumes a drusy structure (Bohemian diamonds, topaz, morion, amethyst). Only ordinary quartz, however, is of interest to the enameller, and this chemically is almost pure silicon dioxide (SiO_2). It is often impure from small amounts of ferric oxide, and, therefore, useless for enamelling purposes. Quartz has a hardness 7, being harder than felspar, and a specific gravity 2·5 to 2·8. It is usually colourless, although often tinted white, yellow, or brown, and possesses a greasy lustre. Quartz is one of the most common minerals, and in granular or crystalline form it is an essential constituent of numerous igneous rocks and crystalline schists—*e.g.*, granite, quartz-porphyry, gneiss, mica schist, etc.—while as sandstone or quartzite it often forms independent masses ; in addition, it occurs in the pebbles of many conglomerates and loose rubble, as well as being the chief constituent of sand (sea, river, and desert sands). It is very infusible, but may be melted at the temperature of the electric furnace.

The following concerns the use of quartz in enamel manufacture :—As a partial substitute for felspar it may be employed for the preparation of ground enamels and the cheaper varieties. In the latter case, the alkali and alumina content must naturally be supplemented by corresponding additions of alkalies and clay. A very peculiar circumstance, which has still not received

adequate explanation, is the practical observation that the quartz is better employed in a not too finely divided condition.

Enamels rich in quartz attack the fusion crucibles fairly energetically with formation of easily fusible silicates. According to Berdels' investigations (*Sprechsaal*, 1909), the specific gravity of quartz decreases with rise of temperature, while its expansion increases. Its active character is lowered with increasing fineness, while its addition makes the enamel fusible with difficulty.

Before use the quartz is tested for the SiO_2 content (which should amount to 97 to 100 per cent.), and for the absence of discolouring ferric oxide (which should not exceed 0·32 per cent.). Whether river sand, quartz crystal, or flint may be employed depends generally upon local circumstances.

If all these varieties exhibit practically the same composition, then experience has established that in most cases it is inexpedient to replace quartz by sand or flint. Here, perhaps, physical processes play an important part. Flint has likewise the chemical composition SiO_2, being found in concretions and as the result of petrefaction in the strata of the Upper Chalk formation ; it also occurs in pebbles, which break with a deeply conchoidal fracture into fragments possessing sharp cutting edges. Its specific gravity is 2·59 to 2·61, and its colour either greyish white to smoky grey, or waxy yellow to brown. Flint possesses a dull lustre, and a crust composed more or less of calcium carbonate.

The following table gives the chemical composition of some varieties of sand (*Sprechsaal Kalender*, 1910). Finally, the remark may be made that where pure sand is to hand, this is employed in the enamel recipe instead of quartz :—

Sand Varieties (Sands from Kaolin, Felspar, Pegmatite, etc.).

Note.—Only those materials are considered whose composition is published in the *Sprechsaal*, or has been ascertained in the Laboratory possessed by the *Sprechsaal*, or communicated by reliable merchants, in which case the source is quoted.

The abbreviations in the analyst column stand for :—
L. d. Sp.—The Sprechsaal Laboratory, C. Bachofen, Coburg.
L. f. T.—Laboratory for the earthenware industry. Prof. Dr. H. Seger and E. Cramer, G. m. b. H., Berlin, N.W., 21.

Description.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	KNaO.	Loss at Red Heat.	Quartz.	Felspar.	Clay Substance.	Melting Point.	Analyst.	Source.
Amöneburg quartzite,	97·46	0·53	1·74	..	..	..	..	..	..	..	35	Wernicke.	Gustav. Westermann, jr., Langerfeld i. Westf.
Amöneburg sand, .	97·90	0·68	0·30	..	..	..	..	..	..	..	..	..	,, ,,
Arloff sand, . .	92·50	4·82	0·23	..	..	n. b.	2·20	..	..	..	..	L. d. Sp.	
Birkenfeld Felsitspar,	81·22	5·71	0·38	..	..	K, 5·75 Na, 1·50	2·10	..	..	..	9-10	Fresenius	Birkenfeld Felspar Works, A.-G., Mainz, Frances Lobstr. 2.
Charlottenburg sand,	96·70	0·93	0·17	..	..	..	..	..	..	..	..	L. d. Sp.	
Dörentrup-Glass sand, O. B.,	99·75	0·035	0·015	..	..	..	..	..	..	..	..	..	Dörentrup Sand and Clay Works, G. m. b. H., Dörentrup (Lippe).
Ebersdorf (Coburg) sand,	89·00	5·98	0·32	0·20	0·31	2·35	1·95	..	..	..	..	L. d. Sp.	
Einberg sand, .	80·46	9·88	1·26	0·64	0·61	4·51	3·02	59·50	27·70	12·80	26-27	L. d. Sp.	
Eisenberg raw sand,	97·21	1·21	0·19		1·21		0·12	93·00	..	7·00	34	L. f. T.	Gösen Clay Works.

Eisenberg washed sand,	98·71	0·59	0·03	..	0·08	0·53	0·18	96·00	..	4·00	35	Störmer.	G. m. b. H., Eisenberg, S.A.
Engelmannsreuth kaolinsand (Pegmatite),	86·28	8·62	0·56	0·12	0·17	2·42	2·10	69·6	14·9	15·5	..	L. d. Sp.	Quartz sand washing firm at Engelmannsreuth.
Engelmannsreuth sand,	98·71	0·46	0·28	..	..	0·24	0·31	..	..	..	35	L. f. T.	„ „
Forauenwald sand, .	92·40	4·11	0·49	0·07	0·32	2·40	0·35	..	..	..	..	L. d. Sp.	Carl Gunderloch.
Freiburg crystal quartz, K. G.,	99·52	0·18	0·09	0·04	traces	..	0·22	..	..	..	..	..	Freiburg i. B.
Freiburg crystal quartz, G. II.,	99·57	0·17	0·12	..	0·24	..	..	..	..	..	..	..	„ „
Freihung pegmatite,	82·99	9·91	0·31	0·16	0·08	5·13	1·35	59·4	30·2	10·4	..	L. d. Sp.	
Fürstenwald glaze sand, I. Schm.,	87·07	6·50	0·20	0·34	1·52	2·30	2·07	74·0	10·70	15·30	..	..	
Grünstädt (Pfalz) quartz sand,	99·57	0·17	0·02	..	0·24	..	..	..	..	..	..	..	Pfälz Schamotte and Clay Works.
Grünstädt (Pfalz) felspar sand,	73·47	13·84	0·34	0·77	0·75	K. 7·87 Na, 2·42	1·41	..	..	..	..	..	A. G. Grünstadt (Pfalz).
Hirschau felspar sand,	69·92	17·74	0·41	0·12	traces	10·40	1·45	6·87	70·44	22·69	16·17	L. f. T.	Amberg Kaolin Works.
Hirschau quartz sand,	92·71	4·38	0·33	..	..	2·33	0·51	81·34	13·78	4·88	..	..	G. m. b. H., Hirschau.
Inowrazlaw sand, .	97·30	1·29	0·56	0·16	0·18	0·12	0·48	..	..	..	..	L. d. Sp.	
Kamenz sand, .	98·32	0·84	0·18	0·12	..	0·56	0·15	..	..	..	..	L. s. Sp.	
Kronach felspar sand,	86·38	7·30	0·62	0·18	0·26	4·32	0·85	64·97	28·27	6·76	..	L. d. Sp.	
Laasdorf quartz sand,	90·55	4·09	0·21	1·30	0·11	3·25	0·52	..	..	..	..	Katz.	G. Riedel & Co., Laasdorf, S.A.D.
Lippstadt sand, .	96·54	1·64	0·48	0·22	..	0·62	0·50	..	..	..	..	L. d. Sp.	

Sand Varieties (Etc.)—*Continued.*

Description.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	KNaO.	Loss at Red Heat.	Quartz.	Felspar	Clay Substance.	Melting Point.	Analyst.	Source.
Löwenstein sand, .	96·96	1·22	0·32	0·08	..	1·08	0·15	..	..	..	..	L. d. Sp.	
Martinroda sand, .	94·00	3·00	little	0·20	..	2·80	..	..	..	..	..	..	
Meifzen glaze sand (after red heat),	91·66	4·50	1·00	0·75	0·86	1·23	(3·26)	..	..	..	..	..	
Metzling sand, .	97·52	1·40	0·36	0·12	traces	0·68	0·17	93·20	49·2	1·88	..	L. d. Sp.	Kollrepp Works Meissen.
Neuhaus sand, .	..	..	0·85	..	..	..	..	61·88	28·40	9·72	..	L. d. Sp.	
Ottensen sand, contains lime,	50·46	2·64	0·16	24·24	1·36	..	CO_2, 20·42	..	..	..	..	L. d. Sp.	
Penzberg sand, .	98·08	1·30	0·16	0·12	traces	0·13	0·13	..	..	..	..	L. d. Sp.	
Quartzbiehl sand, .	97·76	1·36	0·12	0·22	0·07	0·29	0·18	..	..	..	..	L. d. Sp.	
Satzveyer sand, .	92·70	4·63	0·27	..	..	..	2·10	..	..	..	..	L. d. Sp.	
Semlowitz sand, .	90·60	5·05	0·25	0·42	..	3·46	0·30	..	..	..	..	L. d. Sp.	Georg. H. Richter, Themar i. Thür.
Steinfels pegmatite,	..	..	..	..	..	..	..	65·00	35·00	..	..	..	
Sterbfritz sand, .	91·35	6·28	0·22	..	..	0·35	1·80	..	..	..	..	L. d. Sp.	
Tambach sand, .	87·90	5·21	0·81	0·16	0·38	3·84	1·70	..	..	..	..	L. d. Sp.	
Urach sand, . .	86·40	7·48	0·72	0·60	0·47	0·85	3·34	..	..	..	..	L. d. Sp.	
Weingarten sand, .	98·41	0·78	0·35	..	..	0·26	0·20	..	..	..	..	L. d. Sp.	
Weissenbrunn sand,	88·76	7·41	0·16	..	0·32	2·60	0·70	75·90	12·60	11·50	..	..	
,, ,,	94·02	3·20	0·28	..	0·16	1·88	0·46	..	..	..	..	L. d. Sp.	
Wiednitz quartz sand,	99·86	..	..	..	..	..	..	..	..	..	..	..	Wiednitz glass Sand Works, G. m. b. H., Petershain, N.-L.
Wunsiedel felspar, .	64·80	22·20	0·16	0·41	..	9·53	2·38	..	..	..	..	L. d. Sp.	
Wunsiedel pegmatite,	66·82	18·87	0·51	0·36	0·14	K, 8·88 Na, 2·98	1·56	16·95	73·40	9·65	..	L. d. Sp.	

III. FLUORSPAR OR FLUORITE.

Fluorspar is found in nature either crystalline or as granular gangue material. The crystals belong to the regular system with pyramidal habit, although less frequently they occur in octahedral and dodecahedral forms, and are usually large, very beautiful and regular, isolated, or in drusy cavities. Fluorspar is also found in large granular and columnar aggregates, and as dense earthy fluorite. It exhibits cleavage, possesses the hardness 4, and has a specific gravity 3·1 to 3·2. Although often found colourless and perfectly transparent, it usually exhibits a variety of shades—*e.g.*, violet-blue, wine-yellow, green, or grey, and possesses vitreous lustre. The colour very frequently originates from included organic matter (hydrocarbons), and disappears when the fluorspar is heated to redness, leaving behind a white mass.

Chemically, fluorspar is CaF_2 or calcium fluoride, containing 51·15 per cent. calcium and 48·85 per cent. fluorine. According to some authors it melts at 900° C., but recent experiments have placed it at about 1,400° C.*

With gypsum it melts to form a clear bead, which on cooling, however, becomes turbid. On fusion with microcosmic salt (sodium ammonium hydrogen phosphate, $Na(NH_4)HPO_4 . 4H_2O$), corrosive hydrofluoric acid is evolved, as also by treatment with concentrated sulphuric acid (method of manufacturing hydrofluoric acid). Fluorspar is frequently found as a gangue—*e.g.*, in the tin ores of Saxon Bohemia, and Cornwall, in the silver ores of Freiburg, Gersdorf, Marienberg, Annaberg, Münsterthal in Baden, Kongsberg in Sweden, in the gangue of the lead veins intersecting the coal formations of Derbyshire, Cumberland, and Northumberland, Beeralstone in Devonshire; further, in the crystalline schists of the Swiss Alps, in the dolomite of St. Gotthard and in the limestone of Gams in Steiermark. In granular form it occurs in huge masses at Stolberg in the Harz district, Steinbach in Meiningen, and between Gabas and Panticosa in the Pyrenees.

* According to Roff and Plato.

The name fluorspar has originated from its use as a flux for metallurgical and ceramic purposes, a use dating back to antiquity.

The Place of Fluorspar in Enamel Manufacture.—For the general characteristics of fluorspar the chapter on cryolite must be consulted. As to the value of fluorspar in enamels, various opinions have been expressed. Its outstanding property as a flux immediately suggests it to be preferable to more expensive agents, such as boric acid and alkalies, for enamel preparations. Against this, however, must be placed the calcium content, since lime and calcium compounds generally exert an injurious effect upon an enamel. American firms work with unusually large amounts of fluorspar, which is certainly not an advantage to their enamels.

When the fusion temperature is not too high, fluorspar acts as an opacity-producing agent in the enamel, without, however, attaining the same degree of excellence as cryolite or tin oxide. Fused with the enamel at a very high temperature, it gives a colourless, fiery, lustrous glass.

By fusing fluorspar with enamel, part of the fluorine probably disappears as volatile silicon fluoride (SiF_4), according to the equation—

$$2CaF_2 + 3SiO_2 = 2CaSiO_3 + SiF_4,$$

while combination is effected with the silica of the quartz or felspar to form calcium silicate.

When the silicon fluoride is present in small amounts in a reducing atmosphere, it is not improbable * that reaction occurs between the hydrogen of the fuel gases to form silicon hydride and hydrofluoric acid—

$$SiF_4 + 4H_2 = SiH_4 + 4HF.$$

Therefore, during the fusion of an enamel containing fluorspar a uniformly neutral or feebly oxidising furnace is required for avoiding unnecessary loss.

Too great a quantity of fluorspar has an unfavourable influence, since too large an amount of silica is withdrawn from the enamel mixture to form volatile silicon fluoride. Fluorspar, therefore, is more appropriate for enamels poor in silica—*i.e.*, for easily fusible enamels.

* Dr. Berdel, "Fluorite Porcelain," *Sprechsaal*, 1910, (6).

Whether the turbidity effect of the fluoride consists in the separation of insoluble alumina from the felspar of the initial mixture only, as some authors have assumed, has not been finally established. At all events, the fact remains that the amount of fluorine lost during melting is almost wholly dependent on the fusion temperature, its duration, and the quantity of silica present. In cases where fluorspar is used for enamel preparations, the amount should not exceed 5 to 6 per cent. for ground enamel and 2 to 4 per cent. for other varieties, on account of its injurious lime content.

IV. CLAY (Alumino-Silicates).

Although clay does not play that comprehensive part in the enamel industry as in the cognate ceramic branch, nevertheless it is indispensable as a grinding addition. Almost 8 to 14 per cent. of the enamel when ripe for coating consists of this relatively inexpensive clay, and it is consequently of paramount importance to select a suitable enamelling clay. Acquaintance must, therefore, be had with its mode of formation and chemical and physical properties, in order to be in a position to judge the qualitative and quantitative action of the clay according to the modern scientific standpoint. Much defective information is still prevalent with regard to the function of clay in enamels, a fact true for enamelling processes in general.

The ideal clay should possess the chemical formula :—

$$Al_2Si_2O_7 \cdot 2H_2O = Al_2O_3 + 2SiO_2 + 2H_2O,$$

corresponding to

39·6 per cent. Al_2O_3,
46·5 per cent. SiO_2,
13·9 per cent. chemically bound water.

In reality, however, the ratio of silica to alumina is a fluctuating one. The literature on the production of clays by the weathering of felspars is most comprehensive, but only the most important points can be touched upon here.

Weathering is brought about by the influence of physical and chemical forces. Frost and ice action bring about a disintegration of the felspar, which, when further acted on by water, carbonic acid, oxygen, and salt solutions, is chemically changed into new constituents—viz., the formation of calcium carbonate and the partial conversion of lime, iron, magnesia, alkalies, and silica into soluble salts. The initial minerals are usually felspar, augite, hornblende, and mica.

The clay substance is almost always accompanied by impurities, such as quartz, felspar fragments, etc., which sometimes

attain such a proportion that the clay is rendered valueless for specific purposes. As a rule, it may be stated that the composition of the constituent parts varies between exceedingly wide limits.

Clays are usually classified into kaolins, fire-proof clays, slaty clays, pottery clays, marl, loess, and loam. Only the purest varieties—viz., kaolins and fire-proof clays—are of interest to the enameller.

(*a*) **Kaolin.**—Kaolin belongs to those clays which are richest in alumina and most infusible, being usually found in vast beds without definite stratification. It is very soft, friable, and, as a rule, possesses a pure white colour. When levigated it exhibits diminished plasticity and compacting ability. Under the microscope the smallest particles are seen to be crystalline in contrast to other varieties of clay, and this circumstance may explain the reduced plasticity. The production of kaolin by the weathering of felspar may be illustrated by the so-called kaolinisation equation of Forchhammer :—

$$K_2Al_2Si_6O_{16} + CO_2 + 2H_2O = Al_2Si_2O_7 \cdot 2H_2O + K_2CO_3 + 4SiO_2.$$

Potash felspar + carbon dioxide + water = kaolin + potassium carbonate + quartz.

The potassium carbonate, being soluble in water, is dissolved out by rain, etc., while the silica (quartz) is carried away by the mechanical action of the water and deposited as sand in another place. The kaolin usually remains in the place where formed, and the term primary deposit is used. In this case contamination by felspar fragments and quartz occurs to a varying degree, corresponding to the mode of formation. There are kaolins, however, which have been transported from the locality where formed and deposited elsewhere (secondary kaolins).

Often the habit of the original rock may be recognised in the kaolin (*e.g.*, on the Isle of Bornholm from the weathering of granite, and at Muldenstein between Bitterfeld and Jessnitz, where the kaolin has been produced from porphyry). Orthoclase appears to resist weathering better than the other felspars, and, therefore, in Norwegian granite, which is very rich in orthoclase, kaolin is seldom found. Granite and gneiss, which constitute about three-quarters of the known earth's crust, and contain about 50 to 60 per cent. felspar, are accordingly an illimitable store for present and future kaolin deposits. Primary kaolins are purer than secondary (sedimented by floods).

(*b*) **Fireclays.**—The pure clay substance ($Al_2Si_2O_7 . 2H_2O$)—*i.e.*, a clay free from impurities, such as quartz, felspar, and unweathered mineral particles—is more infusible than an impure clay, since the iron, lime, magnesia, and alkalies, which contaminate the latter function as fluxes ; apparently plant residues have led to the formation of carbon dioxide, whose aqueous solution has converted the iron in the progress of time into soluble ferrous carbonate, and the lime into calcium bicarbonate. Both these soluble salts are dissolved out by degrees, and thereby pure white clays are formed free from iron oxide.

(*c*) **Slaty Clays and Clay Slates.**—These are formed by pressure upon stratified plastic clays. While slaty clays still possess a feeble plasticity, the clay slates have completely lost this property.

(*d*) **Pottery Clay.**—This is a plastic clay containing much flux material (lime, magnesia, iron, alkali), and, therefore, incapable of resisting fire. It is coloured more or less by iron oxide.

(*e*) **Marl.**—This is an intimate mixture of clay with calcium carbonate.

(*f*) **Loess.**—A complex arising from the deposition of dust or by river sediments. It is sand-free, feebly plastic, and composed of a mass of mineral fragments, clay, and calcium carbonate, all pulverised to a fine powder.

(*g*) **Loam.**—This is a clay containing much sand and iron oxide, which has generally been formed by the weathering of marl or loess. It constitutes the raw material for making bricks.

The so-called weathering of minerals occurs, not only through the agency of carbonic acid, but also by humus acids,* although these act very slowly.† To elucidate this problem Cornu ‡ has proposed the following theory based on modern physico-chemical views :—The soil consists of so-called colloids (alumino-silicate gels, iron hydrogel, colloidal humus matters), together with not easily soluble crystalloids by weathering. The latter, which are associated with soluble crystalloids, are firmly held (adsorbed) by the colloids. The formation of zeolites and all other decomposition processes, particularly kaolinisation (= production of crystalline kaolin or kaolinite), must be sharply distinguished from weathering.

* Rohland, *Sprechsaal*, No. 49, 1909, p. 708.

† Dr. H. Stremme, *Sprechsaal*, No. 46, p. 670.

‡ "Die heutige Verwitterungs Lehre im Lichte der Kolloid-Chemie." *Sprechsaal*, No. 49, p. 708.

The products of weathering vary according as they arise by atmospheric agency or through organic means (such as contemporaneous activity of the vegetation layer). By the weathering of felspar there usually results an alumino-silicate gel, while by thermal action, on the contrary, a crystalloid, kaolinite, is formed. It is possible that kaolin passes over into kaolinite in the course of time. The microscope is indispensable for distinguishing between amorphous and crystalline kaolin. According to Cornu's * investigations, colloids are very widely spread throughout the mineral kingdom, and their study is of the highest importance for investigating mineral genesis. In every mineral group gels are found, and the alumino-silicate gels are of particular interest, since they have been falsely classified by mineralogists into innumerable species.

The gels of the mineral kingdom are typical products of all normal weathering processes, and Cornu states that for every gel compound there exists a crystalline body of analogous composition—*e.g.*, hydrargillite and bauxite, kaolinite and kaolin.

Cornu's conclusion has been disputed by Stremme † in a noteworthy publication. Stremme believes there is a sharp chemical difference between the alumino-silicate gels, such as allophane, montmorillonite, and halloysite, on the one hand, and kaolinite and the clay substance from clay-forming rocks, on the other. His conclusions are collected together, as follows :—

Where felspar, mica, and minerals related to felspar (*e.g.*, leucite, nepheline) are decomposed by water containing dissolved carbon dioxide—*i.e.*, by weathering—the final decomposition product after addition of water to the pure felspar residue is $Al_2O_3 . 2SiO_2 . 2H_2O$, which is a compound of alumina and silicic acid stable in the presence of carbonic acid, but decomposed by sulphuric, hydrochloric, and hydrofluoric acids, as also by caustic and ordinary alkalies. Hydrochloric acid, however, only brings about a slow decomposition. All the intermediate products between felspar and its pure residue, of which there is a crystalline modification termed kaolinite, are included under felspar clays, in order to have a term expressing their genesis.

The allophane clays must be sharply distinguished from these felspar clays. Numerous minerals have to be classified with the

* *Ztschft. Chem. Ind. Koll.*, Bd. 4, p. 15.

† Dr. H. Stremme, Berlin, "Felspar and Allophane Clays," *Sprechsaal*, No. 7, 1910, pp. 89-92.

former which have been continually neglected by mineralogists. Among these are the water-containing amorphous aluminium silicates deposited in fissures, veins, and hollow spaces by thermal and mineral waters, or arising from the weathering of zeolites and alumina-containing augite. Numerous analyses of these bodies are given in the book referred to above. The clays are there classified into the three groups proposed by Le Chatelier—viz., the allophane group with approximately $1Al_2O_3 : 1SiO_2$, the halloysite group with about $1Al_2O_3 : 2SiO_2$, and the montmorillonite group with $1Al_2O_3 : 3SiO_2$. The composition of these bodies varies within wide limits, and in consequence numerous names exist corresponding to the different contents of alumina and silica—*e.g.*, collyrite, razoumoffskin, cimolite, anauxite, etc. In chemical behaviour they are all similar in being easily decomposed by hydrochloric and sulphuric acids. Their water content is high (up to 50 per cent.) and extremely fluctuating. Besides alumina and silica, they generally contain other components, among which every base and acid known in nature may be represented. In the above-mentioned treatise the endeavour is made to show that in the colloids obtained by precipitation from silicic acid and alumina solutions, adsorbed salts are still present in addition to varying amounts of colloidal silica and alumina. The composition of these natural masses of alumina and silica gels varies, at least in the pure minerals yet known, between $1Al_2O_3$, $0{\cdot}3SiO_2$, and $1Al_2O_3$, $5{\cdot}3SiO_2$. It is, however, extremely probable that they form, on the one hand, a transition to pure colloidal alumina—*e.g.*, to bauxite in part—and, on the other, to pure colloidal silica—*e.g.*, to opal. According to their artificial mode of preparation, they are formed wherever dissolved alumina meets dissolved silica in a medium which is neither too acid nor too basic. In nature, therefore, the probability of their precipitation is enormous, as also their production by the decomposition of augite and zeolites.

Cornu further distinguishes between surface and secular weathering. The former alone leads to gel formation through direct atmospheric agency (alumino-silicate gel and iron hydrogel mixed with the gels of magnesium and iron silicates). Secular weathering operates by water containing dissolved carbonic acid and oxygen being drawn by capillary forces into the deeper strata, whereby after long periods of time not gels but crystalloids (kaolinite) arise, whose composition is analogous to those gels

(kaolin) formed on the surface. In this case a phenomenon occurs which is frequently noticed in chemistry—viz., a complete metamorphosis—when the conditions of temperature, pressure, etc., remain constant, with formation of crystalline bodies, while under conditions similar to those prevailing on the surface, colloidal products preponderate.

Decomposition processes take place which must not be confused with those due to weathering, and which include, among others, kaolinisation, sericitisation, talc and zeolite formation, etc. Under kaolinisation is understood the production of crystalloidal kaolinite from thermally decomposed rock. Roesler assumes this mode of occurrence for all kaolin formations. Gel production on the earth's surface is dependent upon atmospheric conditions—*i.e.*, climate, etc.—so that, while felspar weathers to clay in our zone, it becomes laterite in the tropics (an alumina gel similar to bauxite). Gagel and Stremme * note a case of kaolin formation by the influence of cold acids in the Giefzhübl Spring near Carlsbad.

According to Cornu, the so-called clayey odour is not characteristic of clays, but is also found in certain alumina-free gels, and must be ascribed to adsorbed substances. Rohland † has investigated this problem, and ascribes the odour to organic matter, such as remains of organisms, contained in the clay. Exact information on this point cannot be given by analytical means, since the active substances are present in such extremely minute amounts. Different brands of clay possess varying odours, probably due to differences in the composition of the odour-producing bodies. Zettlitz clay, containing extremely minute traces of organic matter, has only the faintest odour. Rohland has proposed the following theoretical explanation :—

The different varieties of felspar in granite rocks are regarded as alkali-alumino-disilicates, and when subjected to hydrolysis form colloidal silica, besides potassium and sodium hydroxides, which are transformed by atmospheric carbon dioxide into carbonates ; there remains aluminium silicate in its purest form, corresponding to the composition $Al_2O_3 . 2SiO_2 . 2H_2O$, as the residue after the hydrolysing action of the water.

In addition, the very unstable aluminium silicate contained in the alkali-alumino-disilicate complex is decomposed by hydro-

* *Sprechsaal*, p. 78, No. 6.
† *Sprechsaal*, p. 470, No. 32.

lysis into its components, silica and aluminium hydroxide, which are left in the colloidal state. Indirectly also, atmospheric oxygen aids the transformation, as it oxidises the lower oxides of manganese and iron, thereby promoting the hydrolysis. The hydrated oxides of silicon, aluminium, and iron give to the clays their plastic properties, and since very pure kaolin is only feebly plastic, or even not at all, it follows that these colloidal hydrates have been removed by water from the disilicates and transported hence. Accordingly the colloidal nature and coagulation are intimately bound up with plasticity.

While the clay odour cannot be detected chemically, Rohland proposes to transfer it to iron saccharate. The latter is characterised by a certain inactivity—*e.g.*, as opposed to the activity of strongly dissociated hydroxides. Cane sugar presumably forms with the iron ion molecular complexes, which are addition products of the general formula $x[Fe_2(OH)_2] + y[C_{12}H_{22}O_{11}]$. Iron saccharate behaves just like a soluble colloid, being completely held back, and, therefore, itself apparently of a colloidal nature. The clayey odour and flavour are capable of transference to this iron saccharate solution. Rohland, to whom the clay industry owes many valuable scientific publications, has had his beautiful theory attacked by experts no less competent, and the discussion still continues.

In many cases the organic matter in clays is of a fatty character (Königreich, Saxony); and on addition of caustic soda solution is saponified with formation of alkaline or alkaline earth salts of the fatty acids; in one particular Silesian clay the organic matter is present in the form of solid hydrocarbons. Experiments upon the thinning and stiffening of clays by the addition of certain salt solutions (electrolytes) are of outstanding interest, and recent physico-chemical knowledge may solve an important problem in enamel technology—namely, the influence of vehicles (Stellmittel) upon clay additions made during grinding.

In many clays a thinning ensues only after the addition of concentrated salt solutions (electrolytes), while with many others traces of particular salt solutions suffice. In one case the hydroxyl ions in minute concentration bring about an increase in the degree of plasticity, and here the amount and nature of the enclosed organic substances in the clay appear to exert a directive influence. The author has repeatedly emphasized their importance in enamel manufacture, and will return to the subject later.

The — OH ions act upon certain clays from Saxony, partly as a thinning and partly as a setting influence, the former upon the clay substance, the latter upon the organic matter, since the fatty and soapy substances are coagulated by hydroxyl ions in contrast to the clay material itself. Strongly plastic clays are very suitable for thinning purposes. An ideal kaolin, such as that from Zettlitz, which has been levigated almost free from organic matter, can be thinned by powerful agents such as solutions of caustic potash and soda. This may explain the fact that certain enamels are thinned in the working dishes by soda solutions, while others, on the contrary, are thickened. Acids also come in for consideration with this problem.

In many enamel works, soda solution is used for stiffening wet-ground enamels ready for coating. If to such a stiffened enamel a little dilute acid be carefully added, the thin state once more appears. Some enamels exhibit entirely opposite properties, and the author knows firms in which blue enamels have been successfully stiffened by dilute hydrochloric acid. In the latter case soda solution re-establishes thinning. It appears, therefore, that the clay as a grinding addition renders possible the setting of the enamel after the addition of a suitable electrolyte, and that the amount and quality of the organic matter present exerts a directing influence upon the effect produced by the setting agent. The aluminium hydrosols are perhaps transformed by hydroxyl ions into hydrogels, which are precipitated, while in another case the colloid present as gel is changed into the hydrosol condition. Physical chemistry, and especially the ionic theory, may thus be called upon to elucidate many of the hitherto inexplicable phenomena known to the practical enameller.

To understand recent colloidal theory as applied to clay, the terms hydrosol and hydrogel require explanation. Certain bodies—*e.g.*, silicic acid, which are usually thrown down as insoluble precipitates—may remain in solution under special circumstances, and exhibit more or less stable behaviour, although these solutions are decomposed by addition of acids, bases, and salts (*i.e.*, electrolytes), or on heating. These solutions often exhibit beautiful colours by transmitted light, while in reflected light they appear on the contrary to be turbid or dirty. Such combinations are termed "colloidal solutions." If a not too concentrated solution of water-glass (Na_2SiO_3) be prepared,

and to this dilute hydrochloric acid be added, no silica separates out (although concentrated hydrochloric acid produces separation); if this solution be placed in a vessel (dialyser) whose base is formed of a parchment membrane, and this partly immersed in a larger vessel containing pure water, then sodium chloride, one of the decomposition products, diffuses through, accompanied by the excess of hydrochloric acid, while the silicic acid remains behind.

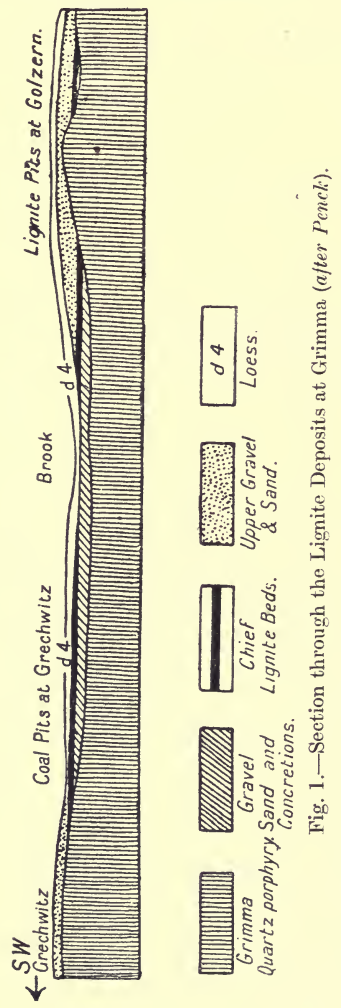


Fig. 1.—Section through the Lignite Deposits at Grimma (*after Penck*).

$$(Na_2SiO_3 + 2HCl + H_2O = 2NaCl + SiO_2 + 2H_2O).$$

If the water be repeatedly renewed on the outside, almost the whole of the sodium chloride may be withdrawn from the solution, while the colloidal silicic acid remaining behind may be immediately precipitated by very small quantities of sodium carbonate as gelatinous silicic acid.

In like manner the hydrates of iron, aluminium, and chromium can form colloidal solutions, since freshly precipitated hydroxides of these elements are soluble in solutions of their colloids (*e.g.*, ferric chloride, aluminium chloride, etc.). In contrast to colloids (possessing a gluey consistency) are the crystalloids which can diffuse through membranes—*e.g.*, sodium chloride solution. According as the precipitates thrown down are again soluble in pure water or not, they were termed by Graham "hydrosols" or "hydrogels," or briefly sols and gels (or also reversible and irreversible hydrosols).

The accompanying interesting sketch (Fig. 1) by Penck in the *Sprechsaal* may give some idea of the characteristic kaolin deposits found in Saxony and Bohemia.

Bischof's Classification of Fireclays.—Bischof divides the clays into seven groups :—

I. *Clays from Saarau* (Lower Silesia).—Coarse clays in slate-like fragments of dark grey colour. To these belong bituminous coal clays, generally of small plasticity, from Scotland (Garnkirk), Wales, Derby, Stourbridge, Sweden, and Saarbrück.*

II. *Kaolin from Zettlitz* (Bohemia).—The crude kaolin from primary deposits is separated from the intermingled quartz sand and mica by levigation. The colour is almost pure white. To this class belong kaolins from Ane (Saxony), Sorzig near Oschatz (Saxony), and China clay from St. Austell, Cornwall. Some inferior fireclays : kaolin from St. Yrieux near Limoges (France) ; Seilitz near Meissen ; Pilsen (Bohemia) ; marl near Halle, etc.

III. *Best Belgian Clay* from Strud-Maiseroul in the Ardennes, being a decomposition product of the carboniferous slates, which is very pure, slaty-blue, and fat. Similar clays are : I*a*. Klingenberg clay (from Aschaffenburg) ; best Müglitz clay (Moravia) ; I*a*. Gottweih clay from Ober-Fuchau near Mautern on the Danube ; clays from Petrikau in Poland, Johnsdorf near Krönau in Moravia, and Jonnec in Croatia.

IV. *Clay† from Mühlheim*, near Coblentz ; the best varieties approach the former classes, and are a dark slaty-blue, very fat, and sand-free. Similar clays are : the better bituminous clays from Nassau, those between Lahn and Sieg, clays from the Ahr district, Lower Silesia, Schwandorf (Bavaria), and Kozlau (Bohemia).

V. *Clays from Grünstaldt in the Pfalz* (Hettenleidelheim), which have a bright blue colour, are free from sand, soaked, and very plastic. Similar clays are found in Löthain (Saxony), Ebernbahn (near Vallendar), Schwarzenfeld (Bavaria), Wildstein (Bohemia), Blansko (Moravia), and also various clays transported by water to become secondary deposits.

VI. *Clay from Oberkaufungen*, near Cassel.—Poor fireclays, bluish-grey, sand-free and very plastic with water. Clays belonging to this class are the poorer varieties of the Mühlheim clays quoted above, the Arthal, Rhine, Nassau, Pfalz, and Belgian clays ; various brands from the tertiary formation in Bohemia, inferior Moravian clays, etc.

VII. *Clay from Niederpleiss*, on the Sieg, which is greenish-

* England exports about 300,000 tons annually.

† Enamelling clays of high quality from Vallendar, near Ehrenbreitstein.

Analyses of Standard Clays.

	Class I. Ia. Clay from Saarau. Typical Bituminous Clay.	Class II. Typical Kaolin from Zettlitz.	Class III. Typical Belgian Clay from the Ardennes.	Class IV. Mühlheim, near Coblentz. Representative of Good Fireclay.	Class V. Grünstadt Ia. A clay similar to kaolin, but from a secondary deposit.	Class VI. A Moderate Lignite Clay from Oberkaufungen.	Class VII. An Inferior Lignite Clay from Niederpleiss.
Alumina, . .	36·30	38·54	34·78	36	35·05	27·97	28·05
Silicic acid chemically bound as sand.	43·84 { 38·94 / 4·90	45·68 { 40·53 / 5·15	49·64 { 39·69 / 9·95	47·74 { 41·00 / 6·74	47·33 { 39·32 / 8·01	57·99 { 33·59 / 22·40	58·32 { 30·71 / 27·61
Magnesia, . .	0·19	0·38	0·41	0·33	1·11	0·54	0·75
Lime, . . .	0·19	0·08	0·68	0·40	0·16	0·97	0·72
Ferric oxide, . .	0·46	0·90	1·80	2·57	2·30	2·01	1·89
Potassium oxide, .	0·42	0·66	0·41	1·05	3·18	0·53	1·39
Loss at red heat, .	17·78	13·00	12·00	11·81	10·51	9·93	8·66
Fireproof, . .	100	70-60	50	45	about 30	20	10
	Absolutely fireproof.	Highly fireproof.	Excellent fireproof.	Good fireproof.	Moderately fireproof.	Fairly fireproof.	Fireproof poor.
	Very lean with water.	Lean.	Very fat.	Extremely fat.	Very fat.	Very fat.	Very fat.

grey, fairly sand-free, very plastic, and containing appreciable amounts of iron and lime. Such clays are found throughout lignite formations together with the superior fireclays quoted above.

ANALYSES OF SOME PLASTIC CLAYS.*

	1.	2.	3.	4.	5.	6.	7.	8.
Silica (SiO_2),	45·99	45·75	45·67	44·27	46·52	47·44	46·62	47·39
Alumina (Al_2O_3),	38·08	35·77	37·42	35·58	38·55	37·21	36·01	36·40
Ferric oxide (Fe_2O_3),	2·44	2·99	1·44	1·15	1·01	1·68	1·39	1·52
Lime (CaO),	trace	..	..	..	..	trace	..	..
Magnesia (MgO),	1·19	0·78	0·57	0·60	0·73	0·79	0·73	0·51
Potassium oxide (K_2O),	2·36	1·24	0·39	0·45	3·47	4·22	3·47	3·96
Loss at red heat,	10·76	13·70	14·41	16·67	10·19	9·69	10·19	9·92

An exact investigation of a number of plastic clays has shown that no appreciable chemical difference exists between the composition of clay substance and the kaolins, but that those clays, possessing a high alkali content, have a small water content and *vice versâ*. The higher the water content the greater is the porosity after firing, whilst a high alkali content causes the clay to sinter more readily. The clays 3 to 6, which are poor in alkalies, are highly fireproof, while 7 and 8, on the contrary, are poor in this respect.

It is well known that only unfired clay possesses the property of maintaining the wet-ground enamel in suspension during the covering process. On firing the clay loses not only its plasticity and its great affinity for water, but also its valuable properties as a grinding addition. On the other hand, the fired clay is capable of increasing the opacity and melting point of the enamel between certain limits. Recently some valuable experiments have been made on the changes taking place when clays are subjected to high temperatures,† and the results are briefly given below.

On firing, the clay first of all parts with its mechanically-bound water (moisture), and then at 950° C. (Seger cone, 010) loses its water of hydration, which is the most important clay constituent being chemically united to it. The clay, therefore, becomes dense, contracts, and sinters, while the water exit brings the clay particles nearer together, and, by aid of the flux present, the whole melts at this temperature.

* Dr. C. Loeser, *Handbücher der Keramischen Theorie.*

† Dr. A. Zöllner, *Tonindustrie Zeitung*, No. 75, p. 793.

Clays and Kaolins.—Tables taken from the *Sprechsaal Kalender* for 1910.

Abbreviations.—L. d. Sp.—Sprechsaal Laboratory, C. Bachofen, Coburg.
L. f. T.—Laboratory for Clay Industry, Prof. Dr. H. Seger and E. Cramer, G. m. b. H., Berlin, N.W., 21.
Sch. L. f. T.—Silesian Laboratory for Clay Industry, Dr. A. König, Bunzlau.
V.-A.—Experimental Station for the Porcelain Manufacture at Charlottenburg.

Description.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	KNaO.	Loss at Red Heat.	Clay Substance.	Quartz.	Felspar	Melting Point. Seger Cone.	Analyst.	Firm.
Altenburg raw kaolin, .	83·40	11·41	0·75	0·13	0·06	0·59	3·66	..	..	..	35	L. f. T.	Altenburg Kaolin Works, G. m. b. H., Altenburg, S.A.
Börtewitz kaolin, . .	56·30	32·28	0·58	traces	0·04	0·17	11·00	82·38	16·59	1·03	35	V.-A.	Gebr. Baensal, Dölau.
Breitscheider clay, No. I, .	54·36*	33·60	1·43	0·21	0·01	0·65	30·06	..	..	..	34-35	Trenzen.	Westerwäld Clay Industry, G. m. b. H., Breitscheid (Dillkr).
,, No. II.,	50·36	35·66	1·64	0·21	..	0·96	11·55	..	..	..	34	Trenzen.	
,, Pa. A.,	46·11	38·27	1·01	..	0·02	0·28	14·61	..	..	..	34-35	Störmer.	
,, Pa. B.,	56·42	30·11	1·04	..	0·07	0·56	12·02	..	..	..	32	Störmer.	,, ,,
Colditz pottery clay, fat,† .	58·96	39·34	1·54	traces	0·16	not detd.	..	..	..	..	35-36	L. f. T.	Friedrich Cramer, Colditz i. Sa.
Ebersdorf blue clay, .	55·04	29·53	2·43	0·11	0·16	0·64	12·38	..	..	..	29-30	L. f. T.	
Eger blue clay, glass, and tile clay,	51·65	31·61	2·44	..	..	1·74	12·94	..	..	..	34	Bischof.	Max. Schmidt, Eger, Bohemia.
Eger pottery and schamotte clay,	45·46	38·10	0·94	0·16	0·24	0·71	14·39	..	..	..	36	L. d. Sp.	,, ,,
Eisenberg kaolin, . .	47·46	36·44	1·32	0·24	0·20	0·85	13·49	92·30	5·87	1·83	..	L. d. Sp.	
,, clay, . .	68·40	21·04	2·28	0·12	0·10	not detd.	7·54	52·70	46·68	0·62	..	L. d. Sp.	
Engelmannsreuth raw kaolin,	86·28	8·62	0·56	0·12	0·17	2·42	2·10	15·50	69·60	14·90	..	L. d. Sp.	
Goesen kaolin, I., . .	48·05	37·14	0·39	0·16	0·11	0·35	13·89	..	..	..	35	Störmer.	Gösen Clay Works, G. m. b. H., Eisenberg, S.A.
,, kaolin II., . .	50·50	35·35	0·28	0·08	traces	0·16	12·60	..	..	..	34	Störmer.	
,, capsule clay, Ia., white firing,	68·88	24·02	0·98	traces	0·15	1·74	5·95	..	..	..	34		
Graupzig crucible clay, .	61·80	22·63	1·37	0·37	..	0·77	12·70‖	..	..	..	..	L. d. Sp.	
Gröden clay, . . .	49·90	34·99	1·20	0·50	0·38	2·02	11·28	82·58	14·49	2·93	34		
Herzogswaldau clay, .	56·24	30·76	1·31	0·21	0·32	1·31	9·85	..	..	..	..	Sch. L. f. T.	Otto Kindler, Naumburg a. Queis.
Hirschau kaolin, . .	48·05	27·41	0·41	..	traces	2·58	11·53	87·01	3·26	9·73	34-35	Störmer.	Amberg Kaolin Works, G. m. b. H., Hirschau.

Hirschau crude kaolin,	..	..	..	..	..	..	..	22·00	60·00	18·00	..	..	,, ,,
,, kaolin,	47·84	38·19	0·70	0·65	traces	0·66	12·20	95·25	1·75	3·00	..	..	Gebr. Dorfner, Hirschau.
Hohburg kaolin,	62·82	26·28	1·04	0·24	0·10	traces	9·56	69·08	30·76	0·16	35	L. f. T.	Hedwigsfreude Co.,
,, pottery clay,	52·87	32·62	1·20	0·51	traces	traces	12·78	85·48	14·50	0·20	35	L. f. T.	Hohburg, near Wurzen.
Kaerlich clay (Coblentz),	43·56	33·04	2·96	1·22	0·65	0·62	18·06	..	..	..	32	L. f. T.	
Kaschka-Mehren glass clay, J. G. Venus.	57·43	29·08	1·24	0·54	0·55	0·79	10·59	..	..	..	32	..	Heinrich Rühle, Löthain-Meissen.
Kemmlitz kaolin,	54·20	32·90	0·29	0·17	0·13	0·49	11·82	84·65	14·84	0·51	34-35	..	Saxon Kaolin Works, G. m. b. H., Kemmlitz.
Kirchheim kaolin,	50·94	33·30	0·51	0·30	..	1·30	13·65	..	..	..	..	L. d. Sp.	
Klingenberg clay,	49·00	32·62	2·45	0·61	..	0·73	14·59	97·15	1·88	0·97	32-33		
Knöbaer clay,	44·36	37·58	1·40	traces	traces	1·18	15·50	..	..	..	34-35	L. f. T.	
Kreisau kaolin (red),	54·80	26·78	3·87 FeO, 0·44	1·30	..	1·74	10·58¶ (+mica)	74·83	24·35	0·82	..	Ahrens.	
Lausigk-Colditz pottery and capsule clay,	58·19	32·16	0·65	0·18	..	traces	9·05	79·86	18·04	2·10	33	..	Baurisch & Junghanns, Lausigk i. Sa.
Lausigk capsule earth,†	68·94	29·29	0·92	0·47	traces	traces	..	..	..	..	..		
Ledicer kaolin, O. A.,	48·22	38·49	0·50	..	traces	not detd.	12·64	90·26	2·58	7·16	..	L. f. T.	Carl Wedell & Co., Pilsen (Bohemia).
,, pottery,	45·46	38·10	0·94	0·16	0·24	0·71	14·39	96·62	0·78	2·60	35-36	L. f. T.	,, ,,
,, kaolin clay, foam sinters,	62·01	25·98	1·80	0·02	0·24	3·02	7·07	..	..	..	26-27	Störmer.	,, ,,
Liboritz clay I.,	54·62	31·80	0·88	..	0·35	1·34	11·02	81·85	9·41	8·74	33-34	Bischof.	New Liboritz Clay
,, II.,	68·66	22·12	0·62	..	0·20	0·93	7·61	60·36	35·34	4·30	32	Bischof.	Works, G. m. b. H., Liboritz-Michelob., in Bohemia.
Libuschin slate clay, I*a*.,†	55·01	44·27	0·45	..	0·18	0·72	..	..	..	..	35	V.-A.	Max. Schmidt, Eger (Bohemia).
Löthain-Meissen glass-ware clay,	60·93	26·31	1·19	0·28	0·21	0·58	10·48	69·38	27·99	2·63	32	..	Heinrich Rühle, Löthain-Meissen.
Löthain-Meissen pottery clay, I., dark,	59·10	27·34	0·76	0·10	0·22	0·43	11·85	72·78	26·53	0·69	31-32	L. f. T.	,, ,,
Löthain-Meissen clay, Rudolf pit,	59·32	28·28	1·41	0·13	traces	..	10·91	78·19	20·99	0·82	..	L. f. T.	
Löthain-Meissen clay, Meissen pit,	60·91	26·48	1·63	0·11	traces	..	8·78	74·68	23·88	1·44	..	L. f. T.	Kollrepp Works, Meissen.

* TCO_2, 0·57.

† Heated to redness.
‖ SO_3, 0·30.

‡ Loss at red heat.
¶ FO., 49.

§ *Sprechsaal Kalender*, 1910.

Clays and Kaolins, Etc.—*Continued.*

Description.	SiO_2.	Al_2O .	Fe_2O_3.	CaO.	MgO.	KNaO.	Loss at Red Heat.	Clay Substance.	Quartz.	Felspar	Melting Point. Seger Cone.	Analyst.	Firm.
Meissen clay, Margarete I.,†	63·98	33·87	1·08	traces	traces	1·07	(11·46)	..	..	..	..	..	Kollrepp Works, Meissen.
Meissen clay, Margarete II.,†	75·49	19·86	1·04	0·75	traces	2·86	(7·27)	..	..	..	..		
Michelober clay, . .	..	..	..	..	..	..	..	75·85	22·85	1·30	..		
Münchhofner kaolin, .	46·64	37·66	0·64	0·52	traces	1·70	13·03	95·57	3·66	0·77	35	L. f. T.	
Neurod slate clay (Graf Magnischer clay),†	50·40	47·80	0·97	0·24	0·21	0·38	..	..	..	..	36	..	Neurod Clay Works at Neurod in Silesia.
Peicherwitz clay, dark blue,	51·12	32·28	2·45	0·88	traces	0·58	12·69	..	..	..	32-33	L. f. T.	Peicherwitz Clay Works,
,, white clay, I.,	66·94	23·30	0·72	0·10	..	0·87	8·07	..	..	..	35-36	..	R. Krause, Schweidnitz, in Silesia.
,, white clay, II.,	64·71	24·76	1·12	traces	..	0·16	9·25	..	..	..	35-36		
Pfälz (Grünstädt) raw kaolin,	82·88	11·15	0·46	0·04	0·14	3·19	2·32	..	..	..	..	..	Pfälz Schamotte and Clay Works.
,, pipe clay, .	58·55	29·86	1·02	0·23	0·62	2·19	10·00	..	..	..	..	..	A.-G., Grünstadt (Pfälz).
,, pottery clay, .	53·17	33·72	0·86	0·07	0·22	0·36	12·03	..	..	..	..	..	,, ,,
,, crucible clay,	47·33	33·05	2·30	0·16	1·11	3·18	10·51	..	..	..	..	..	,, ,,
,, glass ware clay,	47·39	37·24	1·25	0·58	0·53	2·83	10·25	..	..	..	..	..	,, ,,
,, Schamotte clay,	47·81	38·15	0·77	0·21	..	1·26	11·98	..	..	..	..	..	,, ,,
,, clay containing iron,	51·31	20·96	13·11	0·65	2·34	0·59	7·68	..	..	..	..	..	,, ,,
,, lime clay, .	41·71	12·98	4·70	24·46	2·20	1·71	4·83	..	..	..	..	..	,, ,,
,, brand B.F., fat,	55·49	30·94	16·80	0·27	0·11	1·97	9·09	..	..	..	..	..	,, ,,
,, brand B.B., half-fat,	72·65	19·44	0·97	0·19	traces	1·50	4·81	..	..	..	..	..	,, ,,
,, kaolin clay, .	48·05	37·41	0·41	..	traces	2·58	11·53	..	..	..	..	..	,, ,,
,, clay, Ia., highly fireproof,	..	..	..	..	..	..	..	95·03	4·97	..	33	..	Gebrüder Herrmann, Hettenleidelheim (Pfälz).
Pilsen clay, . . .	66·84	23·04	0·52	0·64	0·45	1·09	7·21	66·26	33·02	0·72	27	Wolf. Willort.	
Podersam kaolin, Martin brand.	51·36	34·31	0·74	0·96	traces	not detd.	12·48	..	..	..	35-36		Gebrüder Martin, Lubau, near Podersam (Bohemia).
Pomeisler kaolin, . .	47·27	36·05	0·80	1·70	traces	not detd.	14·35	96·60	3·03	0·37	35	L. f. T.	Benneckendorf & Heiland, Leipzig.

Poschezau kaolin, . .	45·66	39·23	0·80	0·20	0·22	0·83	13·42	99·00	1·00	..	..	..	George H. Richter, Themur (Thür).
,, Caroli-Zeche,	47·10	36·16	1·68	..	0·26	1·40	13·44	..	..	..	..	L. d. Sp.	
Preschen clay, . . .	64·50	19·80	3·37	1·54	0·37	2·74	7·96	61·28	35·02	3·70	..	Bischof.	Tonkontor Preschen (Bohemia).
Rakonitz slate clay,† .	52·50	15·22	0·81	..	0·54	0·50	0·78	99·27	0·73	..	36	L. f. T.	Heinrich Linder, Fichtelberg (Bavaria).
,, crude slate clay,	45·08	39·55	0·15	..	..	..	14·03	..	..	..	35	Störmer.	
Saarau crude kaolin, .	67·09	23·77	0·70	..	..	..	8·50	61·34	38·05	0·61	35	L. f. T.	United Schamotte Works (formerly C. Kulnitz), Saarau.
,, blue clay, fat, .	48·10	35·50	2·50	..	..	..	12·60	96·90	2·40	0·70	35	L. f. T.	,, ,,
Schippach blue clay, .	52·55	31·50	2·19§	0·73	0·19	not detd.	11·73	91·08	6·82	2·10	..	L. f. T.	
Schwepnitz clay, . .	53·03	31·77	0·97	..	traces	2·16	10·82	..	..	..	34	L. f. T.	
Seilitz kaolin, . . .	56·49	30·75	0·48	0·25	0·30	0·96	10·84	80·93	15·85	3·22	..		
Sratoslav kaolin, . .	..	..	..	..	..	..	..	72·45	26·96	0·59	..	..	L. v. Tarty, Tischnowitz.
Tambach blue clay, . .	53·18	25·24	1·64	0·66	0·66	not detd.	17·68	..	..	..	29	L. f. T.	
,, grey clay, . .	54·58	28·00	1·70	1·04	0·55	not detd.	14·08	..	..	..	31	L. i. T.	
Tillendorf clay, . .	69·92	21·09	1·03	0·16	0·18	0·93	6·98	50·49	43·88	5·53	..	L. d. Sp.	
Vranovaer (Moravia) clay, white-grey,	52·42*	33·56	1·17	0·77	0·38	1·28	10·84	..	..	..	33		
Vranovaer (Moravia) clay, dark grey,	52·11	27·73	5·92	0·91	0·57	1·07	12·78	..	..	..	32-33		
Weigersdorf excellent fireproof clay,†	60·07	36·66	1·33	0·48	0·35	1·10	..	..	..	..	33		Weigersdorf Clay Pits, Bautzen.
Wildstein, Ia. kaolin, .	48·10	35·66	1·86	0·22	..	2·65	11·80	92·03	2·60	5·37	34-35	L. f. T.	Werner & Co., Voitersreuth, Bohemia.
,, white burnt pottery,	46·35	38·77	1·11	..	..	0·33	13·44	98·99	..	1·01	35-36	L. f. T.	,, ,,
,, Ia., blue clay, .	54·39	31·35	1·80	..	..	2·47	11·24	96·72	2·22	1·06	33-34	L. f. T.	,, ,,
,, Schamotte clay,	46·70	36·30	2·00	0·20	0·29	1·29	13·44	..	..	..	34	L. f. T.	,, ,,
Wirgeser clay, . . .	51·50	31·11	1·89	0·46	0·07	1·35	13·20	77·36	21·51	1·13	..	L. f. T.	
Zettlitz, Ia., kaolin, . .	46·62	37·68	0·90	0·37		1·10	13·33	..	..	..	..	Bischof.	Carl Knoll, Fischen, near Carlsvad.
,, kaolin, . .	46·13	38·67	0·70	0·08	..	0·11	14·29	99·36	0·13	0·51	..	L. f. T.	Zebisch & Pfeiffer, Zettlitz (Bohemia).

* Traces TiO_2. † Heated to redness. ‡ Schamotte. § Mn_2O_3, 0·13.

Other changes occur, however, at high temperatures besides the above. Le Chatelier and Rohland have established the existence of intramolecular changes, and Prof. Glasenapp, of Riga, discovered by a microscopic investigation that after firing a crystallisation process begins, a fact which led him to the following conclusion :—"All clays become crystalline at high temperatures by dissociation (decomposition) of the clay substance." He explained this phenomenon by supposing that at high temperatures the clay substance is split up into an amorphous, vitreous ground mass and a crystalline portion, the former being a silicate rich in silica whose composition is as yet unknown,

Fig. 2.—Sillimanite isolated by Hydrofluoric Acid from a Wildstein Clay fired at a High Temperature. (Seger Cone 15, 1,430° C.)

while the latter is a silicate rich in alumina (Al_2O_3). The crystalline silicate in porcelain, for example, corresponds in composition to Sillimanite ($Al_2SiO_5 = Al_2O_3 + SiO_2$)—*i.e.*, the molecular ratio of silica to alumina is unity. The isolation of this crystalline component in kaolin has recently been accomplished by Dr. Spitzer, who treated the kaolin with hydrofluoric acid. This crystalline process, however, only appears to begin at a very high temperature (1,470° C.). Sillimanite is insoluble in hydrofluoric acid, and its amount in fired clays fluctuates between

3 to 25 per cent. Highly plastic clays contain only 3 to 5 per cent., while kaolins (lean clays) give a Sillimanite residue of 20 to 25 per cent.

It is obvious, therefore, that this peculiarity of fired clays may not only explain the partial solubility of enamel in hydrofluoric acid (really a corrosion of defective enamelled objects), but also throw a new light upon a defect of frequent occurrence in the enamel industry—viz., the dull appearance which many enamelled wares exhibit after firing. (The crystallising out of Sillimanite from the clay addition could bring about the dull aspect, since every known type of devitrification is a crystallisation phenomenon.)

The Rôle of Clay in the Enamel.—After attempting to give as complete a picture as possible of the present position of chemical, physical, and mineralogical knowledge concerning clays, the part played by clay in the enamel itself will now be considered. The author * has already published a paper on this subject, the substance of which will be given in somewhat revised form.

The increasing importance of the enamel industry has caused its chemistry to be more thoroughly studied during recent years. By the gradual accumulation of scientific knowledge concerning the chemical character of the raw materials on the one hand, and the chemical processes in the separate phases of enamel manufacture on the other, we are to-day in the position of being able to recognise a multitude of manufacturing defects, and to avoid them before disaster ensues. In place of earlier empirical tests and trials, a systematic study has been made of the most favourable composition for different enamels.

The value of practical trials should certainly not be underestimated, but cases are, unfortunately, still numerous where theory is treated with disdain, and defects often remedied after a series of purely empirical experiments. In such cases the scientifically trained expert would arrive at correct results more speedily than the empiricist.

For understanding the mixing necessary for acquiring good enamels, an assiduous study of the raw materials is demanded, in addition to a rich practical experience. Unfortunately, the comprehensive character of our modern enamel works so absorbs the activity of the majority of chemists that problems of the

* Grünwald, "Die Email fabrikation und die Rolle des Tons in dem Email," *Sprechsaal*, No. 19, 1909.

highest interest and importance, which could be solved in part by the staff of a well-equipped laboratory, remain untouched.

Before dealing with the importance of clay in the enamel industry, it is necessary to expose the carelessness often prevailing during the preparation of the enamel. A good enamel requires the greatest care from the instant of choosing and mixing the raw materials to the moment of application (coating). In this respect there still exist defective arrangements in many works. The author has now in mind the exemplary equipment of one of the most famous enamel firms, whose productions deservedly enjoy an extraordinary reputation, which, in spite of manifold competition, still retain their pre-eminence, and their real secret lies in the extreme carefulness exercised during enamel preparation.

Only those brands of felspar and quartz are to be employed whose chemical analyses approach as near as possible to the following :—

Felspar,	SiO_2, . . .	64-66 per cent.
	Al_2O_3, . . .	19-17 ,,
	K_2O, . . .	14-15 ,,
	Fe_2O_3, . . .	traces.
Quartz,*	. . . .	at least 98 per cent. SiO_2.

For first-class enamels the purchase of felspar in lumps is recommended, these being heated to redness and then ground in special drum mills. The mixing of the raw materials should be performed with as small portions as convenient (about 150 kg.), and as intimately as possible. Unfortunately, the necessary attention is not always given to this condition. It is a well-known fact, for example, that blue enamels (coloured by cobalt oxide) appear a much richer blue after prolonged mixing of the raw materials. The blue colour is accordingly not only a function of the amount of cobalt oxide added (on an average 1 to $1\frac{1}{2}$ per cent.), but also of the duration of mixing.

The mixed raw enamel is then melted in the furnace, and,

* The importance of the size of the felspar and quartz grains for various kinds of enamel will be dealt with in a convenient place. Felspar for white enamels should be employed in extremely fine powder; quartz, which promotes the decay of an enamel, should be as coarse as possible, especially for ground enamels.

according to the degree of fusion, a separation into two layers occurs, consisting of an upper specifically lighter portion (borax, alkalies) and a lower specifically heavier. Insufficient crooking (stirring) of the molten enamel causes heterogeneity, whereby different samples exhibit varying compositions and properties. Although these sources of error are well known, yet defects are constantly occurring through the above causes, either by reason of inexperienced workmen or insufficient supervision.

The enamel finally passes to the mill, where further opportunity occurs of appreciably depressing the value of an otherwise excellent enamel either by carelessness or haste. Owing to the extensive trade of many modern enamel works, it frequently happens that the enamel when ground must be used immediately owing to want of space, and this notwithstanding the fact that the beauty and value of an enamel are seriously injured by direct employment after grinding. The older an enamel (within certain limits), and the more carefully it has been purified, the more beautiful and workable it will become, as well as often possessing greater covering power.

Some enamel firms, appreciating these facts, have equipped special elutriation apparatus, and only use a white enamel which has aged for at least fourteen days in special wooden vats (kept scrupulously clean), after grinding and purification. Although the author does not prescribe fourteen days' preservation as an absolute minimum, knowing this to be frequently impossible, yet he recommends three to four days before working up a white enamel after grinding.

The demands, when summarised, are :—

The manufacture of a good enamel requires, in addition to first-class raw materials whose proportions are adapted to the enamel composition, the most careful mixing and melting, scrupulous care at the mill, and an ageing of several days after grinding before use.

Although clay does not command the same prominence in the enamel as in the ceramic industry, yet its function as a grinding addition is always of indispensable importance.

Wet enamelling without a clay addition is simply impossible. The determination of the quantity and origin of the alumina in a modern white enamel is of the highest interest, since this can amount to 10 to 18 per cent. of the enamel when ready for use.

An example will best illustrate this. Commencing with a raw white enamel of the following composition :—

Borax,	62	kg.
Tin oxide,	5	,,
Felspar,	60	,,
Cryolite,	20	,,
Soda, calcined,	4	,,
Saltpetre,	3	,,
White clay,	2·5	,,
Burnt magnesia,	0·2	,,
Fluorspar,	0·1	,,
	156·8	,,

To 100 kg. of the fused enamel are added at the wet mill—

White elutriated enamelling clay,	7	kg.
Tin oxide,	7	,,
Burnt magnesia,	300	gr.

Taking account of the following composition of the raw materials employed, viz. :—

Potash felspar, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$, (neglecting any possible Na_2O content)

K_2O	= 16·81 per cent.
Al_2O_3	= 18·19 ,,
SiO_2	= 64·83 ,,

Natural cryolite $AlF_3 \cdot 3NaF$

Al	= 12·85 per cent.	= 24·27 per cent.	Al_2O_3.
Na	= 32·85 ,,	= 44·12 ,,	Na_2O.
F	= 54·28 ,,		

An enamelling clay of the following composition should be chosen—

SiO_2	= 52·4 per cent.
Al_2O_3	= 33·5 ,,
Fe_2O_3	= 0·8 ,,
Alkali	= 1·5 ,,
Loss at red heat	= 10·9 ,,

The loss which a white enamel suffers on melting amounts, as a rule, to 13 to 20 per cent., in our case 19 per cent., consisting for the most part of water of crystallisation from the borax (47·2 per cent.), and that sustained by the soda, saltpetre, and in part of fluorine, when heated to redness. I must here mention

that a contrary opinion has been maintained from a different standpoint in a short publication elsewhere. I agree with Vondracek,* who states that, after analysing fluorine-containing enamels, the fluorine and silica content practically corresponds to the constitution before melting, and only a very small part of the fluorine volatilises as SiF_4. In addition, the beauty of the enamel does not suffer from the presence of fluorine (between certain limits), and I could never, during many years of practice in the most important European enamelling works, detect any damage worth mentioning, or find that annoyance had been caused in the neighbourhood of the works by fluorine or silicon-fluoride expelled during the melting operations. After the enamel had been fused it passed to the wet mill with the following additions :—

Tin oxide, ...	7 per cent.
White elutriated enamelling clay,	7 ,,
MgO, ...	0·3 ,,

The analysis of the complete enamel after firing gave :—

		Note here that a soft, easily fusible enamel has been chosen of molecular formula :—
B_2O_3,	16·13 per cent.	0·74 Na_2O
Al_2O_3,	14·25 ,,	0·22 K_2O
Na_2O,	15·88 ,,	0·04 MgO
K_2O,	7·37 ,,	0·40 Al_2O_3
CaO,	0·05 ,,	0·65 B_2O_3
SiO_2,	31·31 ,,	1·42 SiO_2
SnO_2,	9·78 ,,	0·80 F_2
MgO,	0·5 ,,	0·19 SnO_2
F,	5·17 ,,	

The total alumina found in the above analysis is made up as follows :—

3·45	per cent.	from cryolite.
7·7	,, ,,	felspar.
3·1	,, ,,	enamelling clay as a grinding addition.
Total, 14·25	per cent.	Al_2O_3.

* *Sprechsaal Kalender*, 1909, p. 34.

Clay is absolutely indispensable as an addition at wet grinding, since without it the finely ground enamel, containing about 30 per cent. water, would rapidly sink to the bottom of the working dishes, and the special operation of enamelling or coating be rendered impossible.

The action of the clay is to maintain the enamel particles in suspension, and in conjunction with the vehicle (Stellmittel) imparts the necessary creamy consistence to the enamel. Further investigation * is needed for explaining the connection between the above fact and the colloidal properties of the elutriated clay.

Since the clay substance frequently amounts to 10 per cent. of the total enamel, the importance of a correct choice of enamelling clay is obvious, especially as from 10 per cent. of relatively inexpensive clay an equal weight of enamel is obtained—*i.e.*, 100 kg. enamel + 10 kg. clay as grinding addition give 110 kg. of finished enamel. It is, therefore, clear that the price of a good enamelling clay should be of no consequence, and only the best brands should be procured.

At the same time clay affords a simple means of regulating the melting point of an enamel as well as the temperature conditions of the furnace, since the melting point of an enamel rises with increasing clay content. For cheap enamels, especially for primary coatings, the clay addition on grinding may amount to 15 per cent. Naturally, such an enamel loses its lustre in consequence of its greater hardness, but gains in opacity. To a certain degree, therefore, clay contributes to the opacity of an enamel, while it confers very favourable physical properties with respect to expansion and durability. All, however, depends on a correct choice of clay, which should not be too fat, yet be as free as possible from iron oxide and calcium carbonate. The absence of the latter is of paramount importance. As a rule, kaolin may not be employed, or only with caution. Should the clay have been heated to redness before addition at the mill, its indispensable properties for our purpose would be lost. Such a clay is excluded as a grinding addition, since with the departure of its water of hydration, its most important property of retaining in suspension the fine enamel particles in the working dishes is entirely lost.

In judging an enamelling clay, it is necessary to know its

* See the author's publication on "Die versteifende Wirküng der Stellmittel," *Keramische Rundschau*, August, 1910.

content of clay-substance, undecomposed felspar, and quartz, and for this purpose the rational and mechanical analyses are sufficient. The behaviour on heating to the firing temperature required by the enamel (about 850° to 950° C.) is of importance. When kaolin is substituted for clay on grinding, a partial contraction of the white enamel may take place on firing. The enamel is then said "to part," and the kaolin employed is termed "too short."

The difference between kaolin and plastic clay lies in the varying properties of the clay-substance, especially regarded from a physical standpoint. Kaolins and clays have been exhaustively studied from an industrial standpoint, although not from that of the enameller, so that here only the observed differences will be dealt with when clay in the form of kaolin is added as a grinding addition. Excellent enamelling clays are found in the Coblentz district (Vallendar, Neuenahr), also at Wirges, Podersam, Rakonitz, and Wildstein in Bohemia.

According to the author's experience, the best clay for enamelling purposes is one with about 51 to 55 per cent. SiO_2, 31 to 34 per cent. Al_2O_3, and an iron oxide content below 1 per cent., with complete absence of $CaCO_3$.

The preliminary treatment of clays before use will now be discussed, and the author would here mention that many enamel firms are still careless in this respect. Enamelling clay before use should be soaked in clean wooden vats, and remain there for several days with frequent agitation until it can pass through a fine sieve. After boiling the clay with water for some time, the calculated quantities for separate grinding additions are taken. Since clay frequently contains impurities of an inorganic or organic nature, the former are removed by elutriation and sieving, the latter by fermentation in wooden vats * with subsequent boiling. If these careful preparations be neglected, defects, after firing in the muffle oven, are often the consequence (blisters, discolourations, etc.).

As a point which cannot be emphasized too strongly, those enamel firms, whose brands are renowned for their beauty and permanence, devote the greatest attention to preparing the enamel. The increased cost is amply recouped by the smaller percentage of damaged wares and the superior quality of the enamels.

* Julius Grünwald, *Theory and Practice of Enamelling on Iron and Steel.* C. Griffin & Co., London, 1909.

For coloured enamels, such as ground and blue varieties, the use of coloured clay (yellow or black) is recommended. The iron oxide content of the latter is not unfavourable to the colour and quality of such an enamel, and, moreover, the use of the cheaper coloured clays means greater economy.

On a previous page it was shown that clay plays a plural rôle, since it not only maintains the suspension of the finely powdered enamel in the water, and thereby makes coating possible, but is also the cause of the "setting" of the enamel when assisted by certain chemicals (vehicles).

From the modern physico-chemical standpoint it is assumed that by the addition of these vehicles, which are all electrolytes (acids, salts, and bases), the hydrosols of the alumino-silicates are precipitated as hydrogels, according to the species of clay employed and the alkalinity of the enamel. With certain enamels (as already mentioned), an electrolyte, such as soda solution for example, may act as a diluent, since the hydrogel present will be transformed into a soluble hydrosol, while acid electrolytes, such as hydrochloric acid, may produce precipitation. In most enamels, however, the alkali and magnesium salts precipitate, while dilute acids have the opposite influence.

When carefully added, a water-glass solution (alkaline silicate) is a good vehicle for special cases, since at the same time it causes the enamel to adhere excellently to the ware before firing. The addition, however, should not exceed ½ per cent., for at 5 per cent. the enamel not only stiffens but solidifies after a short interval.

A brief note concerning vehicles will be given towards the end.

In an economic sense the clay addition is important, since, while inexpensive, it increases the weight of the enamel—*e.g.*, 10 kg. clay added to 100 kg. enamel provides 110 kg. enamel of enhanced value. The amount of clay added fluctuates according to the character of the enamel and the local conditions—*e.g.*, such as the temperature of the muffle oven, etc. The attempt has been frequently made of adding excessive amounts of clay (up to 25 per cent.) to produce a dull, difficultly fusible, white enamel for the primary coat. Such an enamel should be sufficiently opaque to render unnecessary any more expensive opacity-producing agents, since for a second coat an ordinary enamel (glaze), more or less free from tin oxide, is employed as a lustre-imparting coat.

Unfortunately, grave difficulties are encountered with this mode of working, since the finished product readily exhibits blistering, in consequence of the porous sintered character of the first coat, while, in addition, the enamelled ware exhibits an egg-yellow colour, and necessitates a higher firing temperature.

It cannot be doubted, however, that the addition of clay to enamel, especially for cheaper brands, may frequently be higher than has hitherto prevailed. During the fusion of the enamel, the alumina of the clay promotes reaction between the oxides of sodium, potassium, calcium, magnesium, and silicon, thus acting, within certain limits, as an assistant in the formation of compounds between these oxides, functioning as a base or an acid, and thereby neutralising those components present in excess, with consequent preservation of an equilibrium which otherwise would not exist. The alumina thus promotes the formation of a homogeneous mass.* Without the presence of alumina, the enamel would readily absorb carbon from the strongly reducing gases of the furnace with formation of sodium carbide. A not too excessive amount of alumina favourably influences the elasticity, tenacity, and viscosity of enamels, while it tends to increase the surface tension and partly arrests the injurious effect produced by the rapid cooling of the fired enamelled wares. The alumina, therefore, renders the enamel less sensitive to sudden temperature falls, since its coefficient of expansion is reduced and its tenacity increased. Of further importance is the necessity of securing as uniform a distribution as possible of the alumina contained in the clay addition, and for this purpose it is indispensable to elutriate the clay thoroughly before addition, and afterwards to grind it with the enamel as intimately as possible.

* *Trans. Amer. Ceram. Soc.*, 1909, vol. xi., p. 99. L. Friek.

V. BORAX AND BORIC ACID.

Borax or sodium pyroborate, $Na_2B_4O_7 . 10H_2O$, is found in nature as tincal, either in isolated crystals or as crystalline masses on the shores of many Tibetan lakes, also in large crystals often attaining a length of 7 cm. on the floor of the shallow Clear Lake in California, and in the superficial salt deposits of Nevada. Artificial borax, however, is much more important. Tincal usually crystallises in broad, stunted, column-like crystals of the monoclinic system. It is colourless, although usually it possesses a yellowish-green or greyish-white tint, and exhibits a greasy lustre.

The normal chemical formula is $Na_2B_4O_7 . 10H_2O$, corresponding to the following composition :—

16·26 per cent. Na_2O,

35·59 per cent. boric acid (B_2O_3),*

47·15 per cent. H_2O of crystallisation.

Usually, naturally occurring tincal contains impurities in the shape of soap or greasy matter, splinters on rapid heating, swells strongly in the blowpipe, darkening and finally melting to a clear colourless glass with reddish colouration of the flame.

Artificial Borax.—Ordinary or prismatic borax (termed earlier, purified or refined Venetian borax) crystallises in colourless, transparent, six-sided columns, possesses the chemical formula $Na_2B_4O_7 . 10H_2O$, with 10 molecules of water of crystallisation, has a sweetish taste, is not poisonous, and reacts feebly alkaline (red litmus paper turned blue). It dissolves in cold and boiling water as follows :—

* B_2O_3 is really the anhydride of boric acid (boric acid — water). In practice, however, it is termed shortly boric acid.

At	0° C.	100 parts	water dissolve	2·83	parts of crystallised borax.
,,	5°	,,	,,	4·65	,, ,,
,,	20°	,,	,,	7·88	,, ,,
,,	30°	,,	,,	11·90	,, ,,
,,	40°	,,	,,	17·90	,, ,,
,,	50°	,,	,,	27·41	,, ,,
,,	60°	,,	,,	40·43	,, ,,
,,	70°	,,	,,	57·85	,, ,,
,,	80°	,,	,,	76·19	,, ,,
,,	90°	,,	,,	116·66	,, ,,
,,	100°	,,	,,	201·43	,, ,,

The chemical formula shows borax to be a salt of tetraboric acid, which is a pyro-acid only known in its alkaline salts. Tetraboric acid theoretically exists by abstracting 5 molecules of water from 4 molecules of tribasic or ortho-boric acid $B(OH)_3$:—

$$4B(OH)_3 - 5H_2O = B_4O_7H_2.$$

The most important method of producing borax at present is from naturally occurring boric acid, and from several of the borates which occur naturally in huge masses.

In the molten state borax dissolves metallic oxides and salts, forming transparent glasses, which possess characteristic colours —*e.g.*, cobalt oxide gives blue, chromium oxide green, etc. In the air it effloresces superficially, and at a moderate temperature swells, loses water, and melts at 880° C. to a colourless glass. From an aqueous solution of borax of concentration, 30° Baumé (1·26 sp. gr.), warmed to about 70° C. rhombohedral crystals separate, which contain only half the number of molecules of water of crystallisation, and possess the formula $Na_2B_4O_7 . 5H_2O$, corresponding to—

30·8 per cent. H_2O,
47·9 per cent. B_2O_3,
22·6 per cent. Na_2O,

while ordinary prismatic borax (enamelling borax) has the formula $Na_2B_4O_7 . 10H_2O$, corresponding to—

47·15 per cent. H_2O,
36·59 per cent. B_2O_3,
16·26 per cent. Na_2O.

(See later concerning borax manufacture.)

This octahedral variety (jeweller's borax), in consequence of its smaller water and higher boric acid content, is more valuable than the prismatic, but is scarcely ever used for enamels, fluxes, and glasses. It is more compact than prismatic borax.

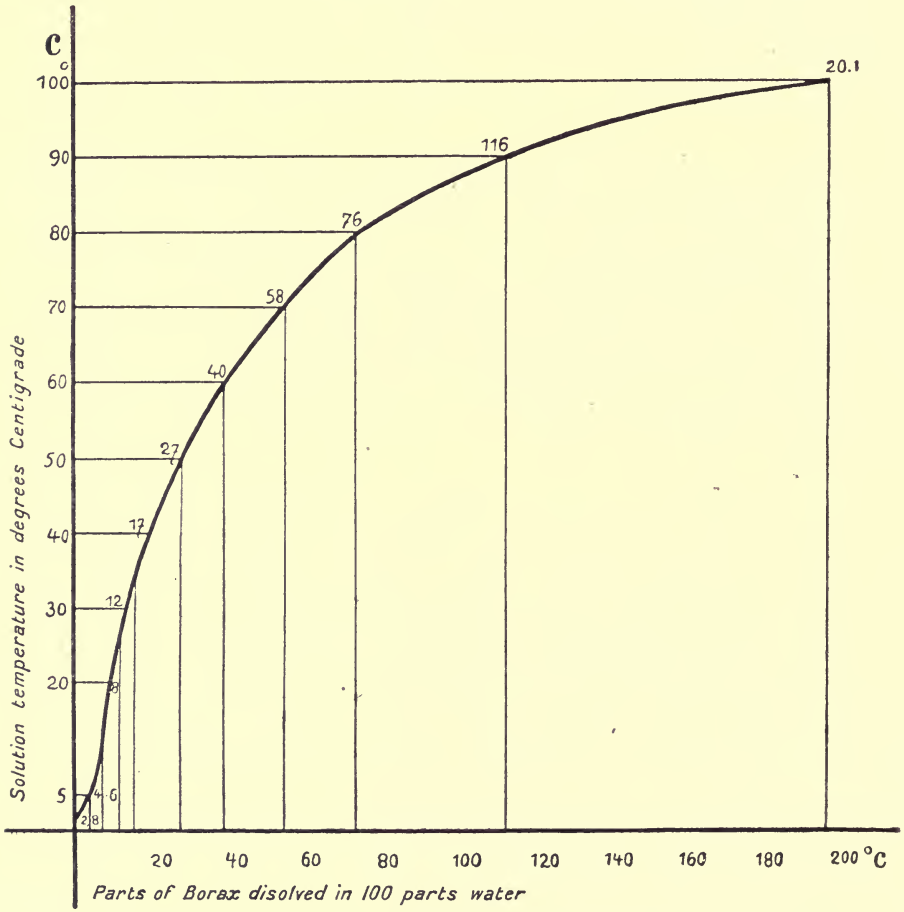


Fig. 3.—Solubility Curve for Prismatic Borax, $Na_2B_4O_7 . 10H_2O$.

Before the manufacture of borax is considered, the crude products themselves must be dealt with. Among these borates are boracite, borocalcite, colemanite, boronatro-calcite. The following table briefly gives the chemical composition of these important minerals :—

The Borates or Boron Minerals.

Mineral.	Chemical Formula.	Number of Molecules.					Composition in Percentages.					
		Boric Acid, B_2O_3.	Sodium Oxide, Na_2O.	Lime, CaO.	Magnesia, MgO.	Water of Crystallisation.	B_2O_3.	Na_2O.	CaO.	MgO.	$MgCl_2$.	H_2O.
Tincal, . . .	$Na_2B_4O_7 . 10H_2O$	$2B_2O_3$	Na_2O	..	..	$10H_2O$	36·59	16·26	..	..	..	47·15
Borocalcite, . . .	$CaB_4O_7 . 6H_2O$	$2B_2O_3$	..	CaO	..	$6H_2O$	52·18	..	20·92	..	..	26·90
Colemanite-Pandermite,	$Ca_2B_6O_{11} . 5H_2O$	$3B_2O_3$	..	2CaO	..	$5H_2O$	50·09	..	27·2	..	..	21·9
Boronatro-calcite, .	$Na_2Ca_2B_{10}O_{18} . 6H_2O$	$5B_2O_3$	Na_2O	2CaO	..	$12H_2O$	45·24	8·83	15·4	..	..	30·79
Boracite, . . .	$Mg_7Cl_2B_{16}O_{30}$	$8B_2O_3$	..	..	6MgO $MgCl_2$	..	62·5	..	..	26·9	10·6	..
Hayesine, . . .	$CaB_4O_7 . 4H_2O$	$2B_2O_3$	..	CaO	..	$4H_2O$	46·11	..	18·89	..	..	35·00

Borocalcite.—This is found in the boric acid lagoons of Tuscany. Its chemical composition corresponds to the formula $CaB_4O_7 . 6H_2O$ (calcium tetraborate), and contains—

20·92 per cent. CaO,
52·18 per cent. B_2O_3,
26·90 per cent. H_2O.

A quite analogous mineral is Hayesine (so-called after the mineralogist, Hayes), which is a biborate of calcium hydroxide—viz., $CaO(B_2O_3)_2 . 4H_2O$, containing

46·11 per cent. B_2O_3,
18·89 per cent. CaO,
35·00 per cent. water of crystallisation.

Hayesine forms nodules (termed Tiza) of delicate, snow-white, crystalline needles, frequently mixed with Mexite, a lime sodio-borate, and Glauberite ($CaSO_4 + Na_2SO_4$); also mingled with sodium saltpetre ($NaNO_3$) on the plains of Iquique in Peru. According to some mineralogists Hayesine should contain 6 molecules of crystallisation water, like the other natroboro-calcites.

Colemanite or Pandermite.—This mineral exhibits monoclinic crystals in 47 forms (according to Jackson and Eakle). They may be short prismatic, or rhombohedral, or at other times long prismatic and rhombic. The hardness is 3·5 to 4, and specific gravity 2·42. The mineral possesses a vitreous to adamantine lustre, is colourless and transparent. Its empirical formula is $Ca_2B_6O_{11} . 5H_2O$—*i.e.*, a lime borate, consisting of—

27·2 per cent. CaO,
50·9 per cent. B_2O_3,
21·9 per cent. water of crystallisation.

In the blowpipe it deflagrates, splinters into fragments, and fuses incompletely. Colemanite is completely soluble in hot hydrochloric acid with separation of boric acid crystals on cooling. It is found in Death Valley, Inyo Co., and in the Calico District, San-Bernardino Co., California, as beautiful large crystals ($\frac{1}{2}$ to 2 cm.) mingled with quartz in inferior druses; the latter occurs also as a soft chalk-like substance (termed Priceite). Pandermite is a hydrated calcium borate very similar to Colemanite (perhaps

only a compact variety of this), and forms snow-white, finely crystalline, marble-like nodules and concretions on the grey gypsum of the Panderma neighbourhood on the Black Sea.

Boronatro-calcite or Natroboro-calcite.—This mineral, which is also termed Merite, is found in the form of white knobby masses, loose in texture, and consisting of fine fluffy fibres. Its specific gravity is 1·8.

It occurs at Iquique (Peru), in the Argentine Province of Jujuy, in the salt marshes of Esmeralda Co., Nevada, and also in South Africa and Nova Scotia. According to Whitfield, the mineral corresponds to the formula $Na_2Ca_2B_{10}O_{18} \cdot 6H_2O$—*i.e.*, a sodium-calcium-borate with 6 molecules of water of crystallisation, containing

15·04 per cent. CaO,
8·83 per cent. Na_2O,
45·24 per cent. B_2O_3,
30·79 per cent. H_2O.

The nodules are mixed superficially with a little common salt, gypsum, and Glauber's salt (Na_2SO_4); when powdered it is sparingly soluble in boiling water, but readily in dilute hydrochloric or nitric acids.

On the West Coast of Africa similar nodules are found, and termed Tincalite. Franklandite from Tarapaca in Chili and cryptomorphite from Windsor in Nova Scotia also belong to this group.

Boracite.—This extremely important raw material for the European borax industry is found in considerable quantities in the Abraum salts of the Stassfurt deposits, crystallising in the regular system, although at ordinary temperatures it is rhombic. The crystals, when completely formed, are scarcely 1 cm. in size. At Stassfurt they occur in druses. The fracture is conchoidal and brittle. It has a hardness 7, and a specific gravity 2·9 to 3.

Boracite may be white, colourless, often yellowish-greenish-greyish-white, exhibiting vitreous, inclining to adamantine, lustre, and is subtransparent to translucent. It commonly shows double refraction, which, however, disappears on heating to 265°, when the crystal becomes isotropic. On warming pyro-electric phenomena occur.

The empirical chemical formula is $Mg_7Cl_2B_{16}O_{30}$, and it may be regarded as—

$6MgO$ (magnesium oxide),
$MgCl_2$ (magnesium chloride),
$8B_2O_3$ (boric acid anhydride).

Or, also, as the acid magnesium salt from 16 molecules of meta-boric acid, HBO_2, in which two hydroxyl groups ($-$ OH) are replaced by two chlorine (Cl)—*i.e.*, $Mg_7H_2B_{16}O_{32}$. Boracite consequently contains—

62·5 per cent. B_2O_3,
26·9 per cent. MgO,
10·6 per cent. $MgCl_2$.

The MgO is often partially replaced by 1 to 2 per cent. FeO (ferrous oxide). Many crystals (*e.g.*, those from Douglashall) contain 7·9 per cent. FeO, traces of water, and calcium sulphate (gypsum, $CaSO)_4$.

Boracite fuses with difficulty in the blowpipe flame, forming a clear yellowish bead, which on setting becomes a white opaque aggregate of crystalline needles. Boracite is difficultly, but completely, soluble in hydrochloric acid.

Crystals are found in the gypsum and anhydrite beds of Lüneberg and Segeberg, also in the Carnallite ($KCl + MgCl_2$) of Leopoldshall, near Stassfurt, and Douglashall, near Westeregeln (Saxony). In the Stassfurt region and other similar salt deposits, boracite is also found in massive ball-like nodules, which are fine-grained, compact, or fibrous, and possess a scanty water content (the so-called Stassfurtite).

A few of the less important borates will only be briefly noticed.

Pinnoite, $MgB_2O_4 . 3H_2O$ (24·39 per cent. MgO, 42·69 per cent. B_2O_3, 32·92 per cent. H_2O), is found in the upper strata of the kainite ($MgSO_4 . KCl . 3H_2O$) region of Stassfurt and Leopoldshall, frequently mingled with earthy boracite or kainite.

Ascharite, $3Mg_2B_2O_5 . 2H_2O$, occurs in pure white lumps in the kainite and rock salt of Schmidtmannshall near Aschersleben.

Szajbelyite occurs in small, snow-white balls, in the granular limestone of Rezbanya (Hungary). Hardness 3·5, specific

gravity 2·7, and chemical formula $2Mg_5B_4O_{10} \cdot 3H_2O$, containing—

54·65 per cent. MgO,
38·35 per cent. B_2O_3,
7 per cent. H_2O.

Hydroboracite occurs in gypsum-like masses in the Caucasus and near Stassfurt, $CaMgB_6O_{11} \cdot 6H_2O$ containing—

13·59 per cent. CaO,
9·67 per cent. MgO,
50·67 per cent. B_2O_3,
26·12 per cent. H_2O.

Lagonite is found as a yellow earthy incrustation at the Tuscan lagoons. It is a hydrous borate of iron, $Fe_2B_6O_{12} \cdot 3H_2O$—*i.e.*, a mixture of boric acid and limonite.

Hambergite.—Rhombic prismatic crystals of a beryllium borate, $Be_4B_2O_7 \cdot H_2O$, or $Be_2(OH)BO_3$, with—

53·3 per cent. BeO,
37·1 per cent. B_2O_3,
9·6 per cent. H_2O.

It is soluble in hydrofluoric acid, and found as a rare mineral at Langesundfjord.

The largest amount of raw material for making borax comes from Argentina as a lime borate. The following information is taken from an expert report by Dr. F. Reichert, of Buenos Ayres :—*

Boronatro-calcite is found in extensive deposits in North-West Argentina, near the Andes. This lime-borate generally occurs, however, in remote places of difficult access, and it is, therefore, necessary, as a partial compensation for the high freightage, to ship a highly concentrated raw product—*i.e.*, a preliminary chemical purification must be made at the place itself. For this purpose many methods find application. In the volcanic region of Puna de Atacama considerable sulphur deposits occur, and these are employed for decomposing the borates.

In Buenos Ayres a limited company has been formed for the purpose of decomposing the Puna borate with sulphurous acid

* "Die argentinuchen Borkalklayen," *Chem. Ztg.*, 1906, No. 15, p. 150.

(H_2SO_3) and calcining the boric acid obtained, thereby bringing it to the market as impure anhydride (B_2O_3). Laboratory tests give 80 to 85 per cent. of boric acid. Dr. Reichert has also endeavoured to bring about the decomposition of the borate by means of the naturally occurring soda which is found in the salt efflorescence of the dry regions of Puna.

The most important localities are :—

(1) The Borateras at Salar del Hombre Muerto.

(2) The Borateras at Salar del Ratones.

(3) The Borateras at Diablillos.

(4) The Borateras at Salar del Pastos Grandes.

(5) The Borateras at Salar del Cauchari.

(6) The Borateras at Salar del Rincon.

(7) The Borateras at the Grand Saline region of the Puna del Jujuy, etc.

The borate beds of the Puna are found in two kinds of layers :—

(*a*) In which the mineral forms a layer of nodular secretions.

(*b*) In which the mineral forms a coherent bank-like deposit of homogeneous character.

The type (*b*) is regional and the most widely spread.

This difference in the mode of occurrence of minerals is very remarkable, since *a priori* conclusions may be drawn as to the quality of the raw product.

The crude borate from the bank-like deposits contains little boric anhydride and more impurities (common salt, gypsum, etc.) than the nodular material, since the beds consist of very porous layers, which absorb any liquids present. It happens, therefore, that these beds lie over saline ground waters, which by infiltration have acquired a quantity of dissolved salts.

The nodules, on the other hand, exhibit a more compact, impervious mass, and, being isolated, hinder the progress of saline waters filtering through the deposit.

The borate bed of type (*a*) affords in general a pure product. Almost all the borate terraces lie on the eastern margin of the Puna del Atacama, at a height of 13,000 feet above sea level. The most favourable places for loading are the towns of Salta and Jujuy on the North Argentina railway.

(1) The most southerly district is the Salar del Hombre Muerto. This is a gigantic salt region possessing borate deposits in different localities on its border, especially on the eastern side at " La Calchaguina " and " La Providencia." It covers an area

of about 5,000 acres with a thickness of about 3 feet. The borate is found in nodules of great purity, with only a moderate salt (common) content. An analysis gave :—

Na_2O, .	9·12 per cent.	$CaSO_4$, .	1·05 per cent.
CaO, .	12·17 ,,	Fe_2O_3, .	0·27 ,,
B_2O_3, .	39·80 ,,	Sand, .	4·34 ,,
NaCl, .	9·30 ,,	H_2O, .	32·92 ,,

Transport and freight charges are unfavourable, since a seven days' march with mules must be undertaken. The loading station is Zwiria, near Salta, and the carriage costs 7 pesos (about 12s. 6d.) per 125 kg. per animal. Fuel and fodder for beasts of burden are scarce.

(2) The borate terraces at Salar del Ratones lie a day's march north from the previous place mentioned, and are still scarcely known. The borate is found in mesenteric bank-like deposits, but poor conditions of working exist. The loading station is Zwiria.

(3) Isolated beds of homogeneous layers of borate are found at Diablillos, about 5 miles east of Ratones, and 13,000 feet above sea level. Lack of communication with the salt zones of a " Salar " has prevented salt accumulation. The borate is, therefore, fairly free from foreign material. A sample contained :—

Na_2O, .	8·70 per cent.	$CaCO_3$, .	4·15 per cent.
CaO, .	9·34 ,,	$CaSO_4$, .	0·53 ,,
B_2O_3, .	30·64 ,,	Fe_2O_3, .	1·34 ,,
H_2O, .	30·92 ,,	Clay, .	4·10 ,,
NaCl, .	6·01 ,,	Sand, .	4·34 ,,

The borate possesses a partially decomposed aspect of a whitish-grey colour, and has an average thickness of 50 to 100 cm.

The whole area is divided into allotments (1 Pertenencia = 250 acres), and up to the present 27 of these have been given as concessions. The workings are not extensive, owing to transport difficulties and freight charges.

(4) The Borateras of Salar del Pastos Grandes lies two to three days' journey north of Diablillos, at the feet of the Nevado del Pastos Grandes (18,000 feet high), and the sulphur mountain, Cerro Azesre (13,000 feet high). At the borders of these saline deposits lie the borate deposits of " La Paz," " Le Blanca Lila," " Aquasamargos," " Sin nombre," etc. The stratification is

similar to that of Diablillos, and has a thickness up to 100 cm. There are extensive deposits of common salt. The mineral contains :—

Na_2O, .	7·67 per cent.	NaCl, . .	17·35 per cent.
CaO, .	9·24 ,,	$CaSO_4$, . .	1·98 ,,
B_2O_3, .	31·05 ,,	Fe_2O_3, . .	1·10 ,,
H_2O, .	28·01 ,,	Insoluble matter,	3·60 ,,

For the time being the borates remain unworked and in the possession of an English syndicate. Freight and transport conditions are more favourable. The stations are Zwiria and Cerillos. The latter is more advantageous, since the greater part of the journey can be done with carts. The freight to Cerillos costs per waggon load of 2,000 kg. for four days' journey along the road to the station 24 pesos paper (about 43s.), and from the deposits to the road, a journey of two days with mules, 2 pesos (about 3s. 6d.). Fodder, water, and fuel are in abundance, but there is a scarcity of labour.

(5) The Antuco deposits are south of the Salar del Cauchari, on the journey along the main Atacama roads to Chili, about 50 miles north of Pastos Grandes and 12,000 feet above sea level. The composition of the mineral varies with the layer, and is found both in banks and nodules. Analysis :—

Na_2O, .	7·88 per cent.	$CaSO_4$, . .	0·63 per cent.
CaO, .	10·04 ,,	MgO, . .	0·42 ,,
B_2O_3, .	32·25 ,,	Fe_2O_3, . .	2·41 ,,
H_2O, .	24·25 ,,	Insoluble matter,	10·19 ,,
NaCl, .	10·03 ,,		

The beds are about 100 cm. thick, and some years ago were mined by the German firm, Boden & Co., the material being shipped to Hamburg. Transport facilities are favourable, and the loading station is Cerillos. Freight for 2,000 kg. is 35 pesos (£3 3s.) for a six days' journey. There is abundant water supply, though pasturage and fuel are limited.

(6) The Borateras of Salar del Cauchari. These deposits are among the most important, being saline beds of gigantic extent with borates at intervals. Large beds are found particularly on the western border, and have been classified into a northern, central, and southern group. All three groups are subdivided into allotments (Pertenencien), which in their totality comprise

perhaps the greatest borate-yielding area. The thickness varies up to 200 cm., but, unfortunately, the beds contain much impurity in the shape of moisture and common salt. The Cauchari borate is classed with the most impure varieties, and as yet only a few positions have been worked by their holder, Schmied, of Buenos Ayres—*e.g.*, the " Porvenir " and " Saltena " mines. An analysis gave :—

Na_2O, .	7·63 per cent.	NaCl, . .	17·83 per cent.
CaO, .	11·60 ,,	$CaSO_4$, . .	1·38 ,,
B_2O_3, .	37·01 ,,	Fe_2O_3, . .	0·70 ,,
H_2O, .	22·68 ,,	Insoluble matter,	1·20 ,,

The nearest railway station for the central and southern group is Cerillos, near Salta. The whole journey from the deposits may be made by carts ; freight costs 36 to 40 pesos for 2,000 kg. (6 to 7 days). The northern group (borates of Olaroz) may be loaded at Cerillos, or a mule journey may be made to the nearer station of Purmamarca, on the Argentine-Bolivian railway. Wages amount to 35 to 40 centarrs per 60 kg. There is rich pasturage and woodland, but the climate is unfavourable.

(7) The borates at Saline Grande (Puna del Jujuy) are still more favourable than those of Cauchari, being of excellent quality and greater extent. It was from these deposits that the Argentine borate export first became commercially important. On almost the entire border of the Saline, borates are found in stratified nodules, in strata which sometimes attain a thickness of 100 cm.

The most important localities are :—

(*a*) Tres Morros, the workings of the " International Belgian Borate Company." Here the deposits are 12,000 feet above sea level, there being excellent transport roads. The crude product is nodular, very pure, and, notwithstanding its saline environment, only a little contaminated. Analysis :—

Na_2O, .	9·03 per cent.	NaCl, .	5·08 per cent.
CaO, .	12·10 ,,	Sand, .	3·05 ,,
B_2O_3, .	36·90 ,,	Clay, .	1·15 ,,
H_2O, .	33·20 ,,		

In consequence of the fall in prices, the Belgian Company temporarily suspended their activities in 1906.

Waggon freight (2,000 kg.) from Tres Morros to Cerrillos is

28 pesos (about 50s.) for a four to five days' journey, while to Purmamarca it is cheaper and shorter.

The crude borate is calcined on the spot in rotatory drums, and thereby converted into 50 to 55 per cent. borate.

(*b*) Triumvirato. On the same border as Tres Morros, but about $3\frac{1}{2}$ miles more south. The raw material and freight charges are as above, and the workings are in English possession.

(*c*) Nino Muerto. On the south-westerly edge of the Saline, and consists alternately of beds and nodules. The salt content is considerable. Analysis :—

Na_2O, .	4·51 per cent.	H_2O, .	24·58 per cent.
CaO, .	8·07 ,,	NaCl, .	29·81 ,,
B_2O_3, .	24·78 ,,	$CaSO_4$, .	4·45 ,,
Fe_2O_3, .	0·70 ,,	MgO, .	4·92 ,,
Sand, .	1·26 ,,		

The thickness is 50 to 100 cm. It is owned by a German mining company, which, however, appears to exhibit little interest in the venture. Freightage to Cerillos as from Tres Morros.

(8) The deposits of Salar del Rincon lie in the central part of the desert, three to four days' journey west from Antuco, and, therefore, offering small inducement. It is under English control, and has sulphur and soda deposits in the neighbourhood which should be of advantage for future chemical operations.

Statistics.—According to the report of the statistical bureau at Buenos Ayres, the export * in 1908 amounted to 3,755,803 kg., valued at 187,790 pes. gold, of which Germany took 880,851 kg., Belgium 299,529 kg., France 340,280 kg., England 1,176,827 kg., and other countries 1,058,316 kg. ; total, 3,755,803 kg. The Belgian company stands at the head of the exporters, followed by the Triumvirato Company and Schmied, the director of "Porvenir."

In 1906 the latter deposit was the only one engaged in the industry. Later statistics—in the year 1908 crude borates and other boron materials were imported into Germany to the extent of 16,166,500 kg., of which 145,200 kg. came from Asiatic Turkey, 9,365,500 kg. from Chili, and 4,955,900 kg. from Peru. At the same time, 539,800 kg. were exported to Russia.

* Loading ports are Colostiné (Province Santa Fé), Rosario, Buenos Ayres.

In 1908 Austria-Hungary imported 4,016,800 kg. of crude borax of approximate value 924,000 kronen, while 157,700 kg. of refined borax, worth 58,000 kr., was imported, and 2,500 kg., worth 1,000 kr., exported.

The Borax Manufacture.—In Argentina the crude product is frequently submitted to preliminary chemical treatment, and thereby concentrated to economise transport charges. The average boric acid content of 35 per cent. is too low for exporting the borate in this condition. In "Tres Morros," and at "Porvenir," the concentration is effected by simple calcination in rotatory drums, the Tola shrub serving as fuel. The calcined product contains between 50 to 55 per cent. B_2O_3. At Porvenir a part of the common salt is removed before calcination by washing.

Other methods are by means of sulphurous acid and soda. The sulphur necessary for the sulphurous acid process is obtained near the volcanoes at Cerro Azufre, Pastos Grandes, and from the Cerro Lacco deposits near Rincon. Both beds occur on the edges of a crater, 15,000 feet high. The difficulties encountered in mining the sulphur are too great, however, to allow the process to be profitable. Dr. Reichert, therefore, does not recommend the sulphurous acid process, although excellent in principle, and the soda process appears to him to be much more practicable. On the banks of the salt lakes occurs a white efflorescence, consisting mainly of common salt, sodium sulphate (Glauber's salt, Na_2SO_4), and sodium carbonate. The soda content amounts to 30 to 40 per cent. In some of the favourable spots, where a continuous supply of soda-containing liquor occurs, the thickness of the deposit often exceeds a depth of 50 cm. The prevailing dryness of the atmosphere in these regions greatly accelerates the evaporation process.

While the Antofogasta soda affords a suitable product for decomposing the borate from the deposits of Hombre Muerto, Diablillos, and Ratones, that from Checce serves the same purpose for Rincon. In Checce, moreover, there is a soda-containing lagoon.

This concludes that portion of Dr. Reichert's report bearing on our subject, and the question of the borax manufacture, which is performed in various ways, will now be considered.

The most simple process, which is carried out in many works, consists in decomposing the boronatro-calcite, boracite, etc., with

soda or soda *plus* sodium bicarbonate. The borate * is dissolved in water contained in large kiers provided with stirrers and steam exits, and a mixture of calcined soda and bicarbonate added (about 6 per cent. of the former and 11 per cent. of the latter, according to the weight of the borate). The solution, which now contains borax, common salt, etc., is pumped through filter presses, in order to separate these from the insoluble and earthy impurities. The clear, hot solution then passes into cast-iron crystallisation vats, in which a series of enamelled plates are suspended. The whole is then allowed to cool slowly and crystallise. The crystals are easily removed from the plates and taken to the centrifuge for removal of adhering water, after which they are ground up and filled into sacks. If large crystals are wanted, the solution is allowed to cool slowly, the crystallisation being delayed by insulating the vat by means of bad heat conductors. If the solution be rapidly cooled, then the so-called octahedral borax (jeweller's borax) is obtained, containing only half the crystallisation water of the former. It is obvious, therefore, that by incorrect manipulation of the crystallisation process, not only would the borax manufacturer suffer loss, since he would deliver for the same price a borax which only contains 30 per cent. of crystallisation water instead of 47 per cent., but also the enameller would be injured, since by employing this water-poor, and therefore borate-rich, product, a defective enamel would be produced. In ordinary borax there is 47 per cent. H_2O, and only 36·6 per cent. B_2O_3, while octahedral borax possesses only 30·8 per cent. H_2O, 47 per cent. B_2O_3, and 22·6 per cent. Na_2O.

If a borax solution be evaporated until its gravity is 30° Bé., and then allowed to cool slowly between 78° and 56° C., octahedral borax will be formed. Below this temperature the ordinary prismatic crystals, $Na_2B_4O_7 . 10H_2O$, separate out, since the earlier octahedral form is slowly transformed into this. If, therefore, octahedral borax be desired (which is unsuitable for the enamel industry), the mother liquor must be poured off when the conditions are 56° C. and 30° Bé ; the latter can then be

* The chemical procedure is as follows :—

$$2(Na_2O . 2B_2O_3 + 2CaO . 3B_2O_3) + 2Na_2CO_3 + 2NaHCO_3$$

Boronatro-calcite — soda — bicarbonate of soda.

$$= 5(Na_2O\ 2B_2O_3) + 4CaCO_3 + H_2O.$$

borax — calcium carbonate.

worked for prismatic borax or evaporated anew and allowed to crystallise. In this way the prismatic (enamelling borax) may be readily transformed into the octahedral by establishing a definite concentration, closing the kier, and pouring off the liquor when the temperature has fallen to 56° C. The chief difficulty, therefore, in borax production is to observe definite temperature and concentration limits before allowing to crystallise.

The preparation of borax has also been essayed from boric acid and soda. 500 kg. of water are run into a kier and raised to the boil, while 20 kg. portions of soda are added, until the amount introduced reaches 600 kg. (222 kg. calcined soda), when the solution is again boiled during the gradual addition of 500 kg. crystallised Tuscan boric acid. Finally, the heating is discontinued, the kier closed, and after 30 hours the clear liquid allowed to flow into shallow crystallisation vessels, where it slowly separates out. By recrystallisation the borax can be further purified.

The mother liquor is used again in the process until it becomes saturated with certain salt impurities, when it is discharged unless by-products are desired.

A recent method, concerning which no works' reports are to hand, depends on the decomposition of boric acid salts by sodium sulphate. Although this process has undeniable interest, only a brief description may be given here.* In previous processes the borax is prepared by first converting the calcium and magnesium borates into boric acid and treating this with soda, or by prolonged boiling of finely powdered calcium borate with soda solution; now G. E. Bailey proposes to mix the above-named boric acid salts with sodium sulphate (Glauber's salt, Na_2SO_4) in molecular proportions, and to heat them to redness in a special furnace without, however, fusing the mass. If Colemanite be taken as the raw material, then the decomposition proceeds according to the following equation :—

$$2Ca_2B_6O_{11} + 3Na_2SO_4 = 3Na_2B_4O_7 + 3CaSO_4 + CaO.$$

Colemanite Glauber's salt borax gypsum lime.

The reaction ensues rapidly, the final mass being then extracted with water, and the clear borax solution allowed to crystallise.

* Amer. Patent, 911,695, *v.* 9th Feb., 1909. G. E. Bailey, "Los Angelos, California," communicated by A. Stevenson, Los Angelos. *Chem. Ztg. Rpt.*, 145.

The following apparatus (Fig. 4) serves for carrying out the operation.

The materials are fed into the rotatory furnace through opening 9. The heating flame (oil gas) enters by opening 10. The raw materials for heating are charged by the transport waggon 28, and thoroughly mixed by the projections 26, provided in the lining 25 ; after the reaction the mass is transported by the waggon 29 into the extraction vessel 3, where it is treated with boiling water, which enters by the pipe 4. The openings 15 serve for drawing off the clear solution, and 16 for removing the

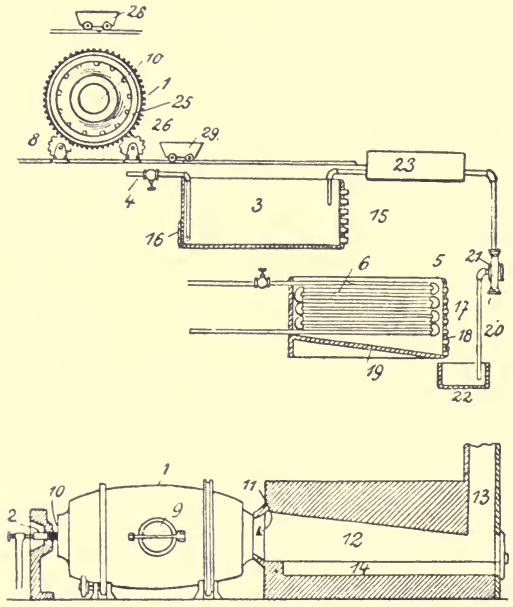


Fig. 4.—Rotary Furnace for Borax Manufacture.

insoluble residue (gypsum and lime). The solution is then cooled to 0° C. in the pan 5, which has a sloping base 19, and is provided with a cooling system 6 ; opening 17 serves to draw off the liquid, and the opening 18 for removal of the borax separated out. The liquor separated from the borax is withdrawn from the pan 22 by the pump 21, and led by the pipe 20 into the hot chamber 23, from which it passes into the extraction apparatus 3. The hot chamber is heated by the fuel gases, which are forced by the chimney 13 through the chamber 12 *via* 11. In this chamber is

an evaporating pan 14, which serves to bring the borax solution to the crystallisation point if cooling pan 5 has been omitted. By the chilling process borax is obtained as a fine powder, so that the subsequent grinding after a slow crystallisation is not necessary.

The Rôle of Borax in Enamel Manufacture.—Crystallised enamelling borax possesses the formula $Na_2B_4O_7 . 10H_2O$, corresponding to—

16·26 per cent. Na_2O,
36·59 per cent. B_2O_3,
47·15 per cent. H_2O of crystallisation.

In glazes, fluxes, and enamels it acts as a flux, in consequence of its ready fusibility. Should other alkalies be employed as fluxes, such as soda and potash, their moderate use is advisable. In glass manufacture some special brands are produced, in which a part of the silica is replaced by boric acid (borosilicate glazes). Borax lowers the melting point of the enamel, and allows of its regulation within certain limits. Although an acid function is generally ascribed to boric acid anhydride, since enamels may be defined as solid solutions of silicates and borates (boric acid salts of alkalies, alumina, and lime), it is not impracticable to regard boric acid as possessing an amphoteric nature—*i.e.*, one functioning both as base and acid—for example, as a base towards strong acids and as an acid towards strong bases.

The position of the element boron in the periodic system, in which it forms the transition from the most acid-forming metalloids to the most basic-forming metals, accounts for the difficulty of fixing the true chemical part played by boric acid in enamels. In its compounds boron resembles the metals beryllium, aluminium, and scandium.* C. B. Binus † has established that the boric acid—*e.g.*, in frittered glaze—was not able to replace the silica, and expresses the possibility (already put forward by Purdy and Fox) that the action of the borax in glazes is similar to that of the aluminium, since both inhibit devitrifications (crystallisation). In support of this theory Binus puts forward the following proof :—

(1) Seeking to establish that B_2O_3 unites directly as base

* Richter's *Lehrb. d. anorg. Chemie*, 1906, p. 278.

† *Trans. of the Amer. Ceram. Soc.*, vol. x., p. 158; *Sprechsaal*, vol. xxxiii., 1909, p. 480.

with SiO_2, he melted both together in the molecular proportions of 1 : 2, using Seger cone 6, and attained a milky-white glaze, which was decomposed, wholly or partly, by water. The cause of the opalescence in glazes observed by Purdy and Fox is supposed to be due to the borosilicate arising, since this is suspended in the glaze, and on cooling crystallises out.

A reaction actually occurred when melting a mixture of boric acid and silica at a sufficiently high temperature (1,100° to 1,200°) in a platinum crucible, which was indicated by a sudden rise of temperature. According to Binus, the fusion of $B_2O_3 + 2SiO_2$ is, therefore, a similar process to the fusion of $Na_2O + 2SiO_2$ or $CaO + SiO_2$.

(2) Binus investigated the part played by borax in the glazes, and, in his opinion, this actually functions as a base, serving to replace the aluminium either whole or part, in addition to its particular influence upon the melting point of the glaze. This opinion is in direct opposition to the hitherto accepted ceramic outlook, although the exhaustive experiments made by Binus lend much support to his theory. According to him also, the B_2O_3 reinforces the action of the alumina as regards viscosity. He shows, for example, that the B_2O_3 in frittered glazes only functions as a base, if the assumption of the bisilicate law be made. This interesting question, however, still calls for further investigation.

Enamels containing boric acid are readily fusible and lustrous, although, hand in hand with the smaller or greater borax content, they give a longer or shorter durability. The greater the boric acid content in the enamel, the further this is removed from the characteristic permanence of glazes towards acids and alkalies.

No enamel exists, however, which bears comparison in this respect with glass. The so-called acid-resisting enamels, which contain little of such fluxes as boric acid and alkalies, are, therefore, rich in silica, and are fairly permanent up to a certain point, although such enamels are feebly lustrous and difficult to manipulate.

The rôle of enamels is quite another to that of glass proper. The percentage borax content in 100 kg. of the crude mixture fluctuates in good trustworthy enamels between the following limits :—

Ground enamel for sheet iron,	30-45	per cent.,	usually	35-39	per cent.		
White	,,	,,	20-34	,,	,,	24-27	,,
Blue	,,	,,	18-29	,,	,,	23-29	,,
Acid-proof	,,	,,	13-23	,,	,,	24-29	,,
White for pottery,	.	.	21-40	,,	,,	34-40	,,
Powder white for pottery,	.		40-44	,,			

The German borax consumption for enamels may be roundly estimated at 10,000,000 kg.

Useful Hints on the Use of Borax in Enamel Manufacture.*—Borax is never stored in the open, owing to its deliquescent properties, whereby it alters in weight, and in consequence may introduce error during mixing. For the same reason, the moisture content of a borax consignment is determined on arrival in order that compensation may be claimed from the dealer if necessary. Up to 6 per cent. moisture may be determined in such consignments, and, therefore, no further remarks are necessary as to the importance of such a fact in large enamel works. The borax is preferred in a sufficiently finely-powdered condition. In works where borax is produced, efficient drying is accomplished by means of the centrifugaliser followed by grinding. The finer the borax powder and the more intimate its admixture with other enamel components, the greater is the homogeneity, and, as a consequence, the beauty is enhanced.

In general it is inadvisable to prepare borax in the enamel works itself, as manifold disturbances may arise. These raw materials are not yet the monopoly of syndicates, for a sufficient number of outside merchants still deal in these compositions, so that a too-detailed manufacture of separate products (see under *Tin oxide*) may prove uneconomical. Here, of course, arises the question of proportion between division and specialisation of work. That chemical firm, which is employed more or less exclusively with borax manufacture or the production of metallic oxides and pigments, etc., will be most capable of rendering efficiency and meeting competition.

Boric Acid.—A distinction must be made between natural and artificial boric acid. The natural variety termed " Sassolite " crystallises in the triclinic system, usually as scaly or fibrous six-sided tables. The crystals are loose or united in crusts and stalactitic aggregates, cleavable, soft, flexible, colourless, although

* See the author's *Theory and Practice of Enamelling on Iron and Steel*, p. 7. C. Griffin & Co., London.

usually possessing a yellowish-white tint, and translucent with pearly lustre.

Boric acid has a greasy feel, tastes slightly acid and bitter. Its chemical formula is $B(OH)_3$ or H_3BO_3, and it may be regarded as consisting of 1 molecule B_2O_3 and 3 molecules of water—viz., $B_2O_3 . 3H_2O$. Pure boric acid, therefore, contains—

56·39 per cent. B_2O_3,
43·61 per cent. H_2O.

Boric acid is easily soluble in boiling water, but somewhat sparingly in cold, while it melts in the blowpipe flame with production of a characteristic light green colour.

Boric acid is found free in nature in some volcanic regions—*e.g.*, in Tuscany (at Lardarello) and Sasso—where it is present in small amounts in the steam which escapes from the earth (from fumaroles on the Isle of Volcano, and termed soffioni). This steam condenses in small natural lagoons, or is conducted into walled basins filled with water. The boric acid crystallises out on evaporating the aqueous solution.

Artificial boric acid is obtained by treating hot borax solution with nitric acid, and separates from the hot solution in colourless, lustrous scales.

One part of boric acid dissolves in 24 parts of water at 14° C., and 1 part of boric acid dissolves in 3 parts of water at 100° C.

The solution reacts weakly acidic, moist turmeric paper being coloured reddish-brown after drying. Part of the boric acid is volatilised when a solution of it is boiled. The boric acid $[B(OH)_3]$ on heating loses one molecule of water at 100° C., becoming metaboric acid (HBO_2), while on further heating at 140° C. the meta acid is transformed into pyroboric acid ($H_2B_4O_7$). On heating to redness the final dehydration occurs and boron trioxide results. The latter is a fusible vitreous mass of specific gravity 1·8, and only partially volatile at very high temperatures. In water the fused anhydride again dissolves to form boric acid.

While most metallic oxides are soluble in the boric acid melt, the following appear either sparingly soluble or insoluble, viz. :—The oxides of beryllium, aluminium, chromium, yttrium, erbium, silicon, zircon, thorium, tin, molybdenum (trioxide), and uranium.*

* Gürtler, *Sprechsaal*, 1907, No. 45.

According to the same writer a part of the oxide changes on melting with the anhydride to form the lower oxide with evolution of oxygen—*e.g.*, uranium trioxide, chromium trioxide, the sequioxide and higher oxides of manganese, cerium oxide, thallium oxide, and those of the noble metals. Antimony pentoxide passes into solution as trioxide with evolution of oxygen, while with tin compounds there is always a decomposition into tin and tin dioxide.

Boric acid may be easily detected chemically in the wet way, by heating a sample with sulphuric acid, adding alcohol, and then igniting the mixture. The volatile boric acid colours the alcohol flame a very pure green.

The part played by boric acid in the enamel industry has already been described fully in the chapter on *Borax*. Boric acid, however, finds only limited application in enamel manufacture at the present time. The method of replacing 100 kg. borax by the corresponding quantities of boric acid and alkali in an enamel recipe will next be described.

100 kg. borax consists of

16·26 per cent. Na_2O,
36·59 per cent. B_2O_3,
47·15 per cent. H_2O.

Boric acid consists of

53·39 per cent. B_2O_3,
43·61 per cent. H_2O.

Natural Tuscan boric acid (Sassolite) frequently contains only 88 per cent. of pure boric acid, $B(OH)_3$. The calculation is based on the assumption that we have to deal with pure 100 per cent. boric acid (artificial boric acid). Since 100 kg. borax contain 36·59 kg. B_2O_3, this quantity corresponds to 68·53 kg. boric acid ($100 : 53{\cdot}39 = x : 36{\cdot}59$). The 16·26 kg. of Na_2O in the borax are contained in 28·13 kg. of calcined soda, since 1 kg. calcined soda = 0·585 kg. Na_2O.

In order, therefore, to replace 100 kg. borax, we must mix 68·53 kg. pure boric acid and 28·13 kg. calcined soda. A simple calculation from the standpoint of price shows whether, in individual cases, the replacement of borax by boric acid and soda would be economical. Boric acid is very trustworthy for certain

colour enamels, since the development of colour from the pigment is more pronounced.

The excellent volumetric methods of M. Hönig and G. Spitz * are recommended for the quantitative estimation of the boric acid and borates in enamels.†

* *Zeitschrift für angewandte Chemie*, 1896, part 18.

† See further, Gooch and Jones, *Zeitschrift für angewandte Chemie*, 1899, vol. xix., p. 417; or Classen, *Ausgewählte Methoden der analyt. Chemie*, 1903, vol. ii., pp. 592-594; or Arndt, *Chem. Ztg.*, 1909, No. 80, p. 725.

VI. CHEMICAL TECHNOLOGY OF CRYOLITE AND ITS SUBSTITUTES, SUCH AS SODIUM SILICOFLUORIDE; ALSO THE FUNCTION OF CRYOLITE IN ENAMEL MANUFACTURE.

Cryolite will first be discussed from a mineralogical,* chemical, and technical standpoint, before its importance as a white opacity-producing agent and as a flux in enamel manufacture is dealt with.

Natural cryolite, which belongs to the anhydrous double fluorides of the mineral kingdom, occurs in cube-like monoclinic crystals bounded by three sets of sides almost at right angles, and exhibits cleavage parallel to these sides. At first glance cryolite gives the impression of a quadratic tabulation of compact masses, which are sometimes found in step-like formation. Cryolite is a brittle, colourless, greyish-white often yellowish to red, mineral of hardness 2·5 to 3 (therefore fairly soft); it has a specific gravity of 2·95 to 2·97, and melts at about 1,000° C.

Many American varieties are pale-red or greenish in colour, but the black Greenland cryolite is a curiosity. In all cases this colour disappears on heating. The crystals are often covered with an easily detachable skin containing a little ferrous hydroxide. Cryolite usually exhibits vitreous, sometimes a pearly, lustre, being generally only feebly translucent and greasy to the touch. It is slightly double refractive to light. Its chemical nature is expressed by the formula Na_3AlF_6 or $3NaF \cdot AlF_3$ (*i.e.*, 3 molecules sodium fluoride + 1 molecule aluminium fluoride), and in its purest form contains 32·79 per cent. Na, 12·85 per cent. Al, and 54·36 per cent. F; or, otherwise written, 60 per cent. NaF and 40 per cent. AlF_3.

Before the blowpipe it fuses very readily to a white enamel-like mass, colouring the flame reddish-yellow, and giving the fluorine reaction on glass. This test consists in taking a sample of the cryolite or of any fluoride and warming it with concentrated sulphuric acid in a small platinum crucible; the latter is

* From Zirkel-Naumann's *Elem. d. Mineralogie*, 1907.

Table giving the Theoretical Composition of Cryolite and Allied Minerals.

		Na.	Al.	F.	Li.	K.	H_2O.	Si.	Ca.	Occurrence.
Cryolite, . . .	$3NaF . AlF_3$	32·79	12·85	54·36	..	..	..	..	..	Ivigtut at Arksutfjord, Pike's Peak in Colorado.
Cryolithionite, . .	$3NaF . 2AlF_3 . 3LiF$	18·5	14·5	61·22	5·66	..	..	..	..	Ivigtut, Pike's Peak.
Chiolite, . . .	$5NaF . 3AlF_3$	24·8	17·5	57·7	..	..	..	..	..	Miask in the Urals.
Hierutite, . . .	$2KF . SiF_4$	..	..	51·9	..	35·4	..	12·7	..	Fumaroles on the Isle Volcano (Hiera).
Prosopite, . . .	$CaAl_2(F . OH)_8$	..	14·1	39·8	..	..	..	..	10·4	Pike's Peak, Torvel Co., Utah.
Pachnolite, . . . Thomsenolite, . .	$NaF . CaF_2 . AlF_3 . + H_2O$	10·3	12·2	51·5	..	..	8·1	..	17·9	Ivigtut (Greenland), Pike's Peak.
Ralsonite, . . .	$(Na_2Mg)F_2 . 3Al(F . OH)_3 + 3H_2O$	9·4	16·6	43·00	..	..	11·1	..	Mg = 4·9	Ivigtut (Greenland), Pike's Peak.

covered with a glass plate having a thin wax coating, along which a fine line has been drawn by a wood point to bare the glass in places. After a short interval the glass will be etched in these places. According to Nickles, it is better to cover the crucible with a quartz plate, because the sulphuric acid vapour itself acts upon glass. Cryolite fuses very readily on charcoal, forming a decomposition residue of alumina (Al_2O_3), which is coloured blue by cobalt solution (solution of cobalt nitrate). Cryolite is easily soluble in borax and microcosmic salt ($NaNH_4HPO_4$). Concentrated sulphuric acid dissolves it with formation of hydrofluoric acid (HF).

Localities where found are Evigtok (Ivigtut) at Arksutfjord in South Greenland (mixed with Pachnolite = $NaF \cdot CaF_2 \cdot AlF_3 \cdot H_2O$), where it forms an almost rectangular stock in the gneissic mountains, often mixed with iron and copper pyrites, lead glance, spathic iron ore, and quartz, and often also containing beautiful crystals of columbite and tinstone. At Miask in the Urals it accompanies chiolite ($5NaF \cdot 3AlF_3$), while it is found in a quartz gangue among the granites near Pike's Peak, Colorado, with other fluorides as in Greenland.

Similar minerals often accompany cryolite, such as chiolite, pachnolite, cryolithionite (see previous table).

	Analysis of a Natural Cryolite.	Analysis of an Artificial Cryolite.
Al, . . .	12·99 per cent.	13·30 per cent.
Na, . . .	32·29 ,,	32·50 ,,
F, . . .	52·49 ,,	52·20 ,,
Fe, . . .	0·22 ,,	0·02 ,,
SiO_2, . . .	1·74 ,,	1·00 ,,
H_2O, . . .	0·27 ,,	0·98 ,,

The Winning of Natural Cryolite.*—Since almost all natural cryolite comes from Greenland, it is of interest to go further into

* The chemical firm, Oeresund, at Copenhagen, who are the well-known vendors of natural cryolite, have communicated to the author in a private letter that purely natural cryolite when ground contains about 98 per cent. and never less than 97 per cent. of sodium-aluminium fluoride, the rest being quartz (silica).

As this statement is not in exact agreement with other analyses of natural cryolite, the author will readily give space for correct information, since contamination of natural cryolite by quartz may conceivably fluctuate, within certain limits, according to the care and method of sorting.

the details of winning, and so the following abstract has been taken from a publication by C. F. Jarl.*

The total cryolite demand is supplied by S.W. Greenland at Ivigtut, 10 km. from the S. side of Arksutfjord, and in the same latitude as Bergen.

Here cryolite outcrops on the surface. The mineral was brought to Denmark for the first time towards the close of the eighteenth century. A chemist, P. C. Albigaard, established in 1800 that cryolite contained hydrofluoric acid, alumina, and alkalies, or, in the language of those days, fluorspar acid, alum, and plant ash. From him the Portuguese mineralogist, D'Andrade e Silva, obtained samples of the mineral, to which he gave the name cryolite (ice-stone), since under water it resembles ice which has frozen rapidly. In 1850 Jul. Thomsen, then assistant in the laboratory of the Copenhagen Polytechnic, undertook experiments to determine whether the mineral, which he recognised as sodium aluminium fluoride, was applicable for the preparation of soda and alum, which were then valuable products. The decomposition experiments with burnt lime under dry as well as wet conditions were successful, and formed the foundation of the cryolite industry. Thomsen took out the first patents, and so found economic use for the minerals from inhospitable Greenland. Simultaneously, Howitz, a gas-works' director, working with him, found that cryolite could be employed for the preparation of iron enamels. Thomsen's investigations for utilising cryolite in the earthenware and cement industries met with no success. The principal demand at Copenhagen in those days was for soda crystal, and in 1855 Thomsen began to erect the Oeresund Works, and there commenced business on his thirty-third birthday,—Feb. 16th, 1859. According to Thomsen's researches, cryolite was a fluor-aluminium-fluor-sodium-compound, which underwent the following reaction with $CaCO_3$:—

$$2AlF_3 . 3NaF + 6CaCO_3 = Al_2O_3 . 3Na_2O + 6CaF_2 + 6CO_2.$$

The process was first carried out by heating chalk and cryolite to redness in retorts similar to those used in gas works, but later Thomsen designed a special furnace for the operation. After four hours' heating the mass is allowed to cool, and then subjected to a systematic lixiviation, whereby the fluorspar remains

* *Ingenioren*, 1909, vol. x., pp. 75-80. See report in *Chem. Ztg.*, 1909. "Chemical Report," p. 260.

behind, and a fairly concentrated solution of $Al_2O_3 . 3Na_2O$ is obtained. This is precipitated by the carbon dioxide from the furnace process, whereby an hydrated alumina together with some soda is obtained, and a clear solution of soda, which can be evaporated and crystallised. The extracted alumina is dried and sold or worked up for alum. On the model of the Oeresund Works, Thomsen erected others in Pittsburg, Mannheim, Prague, Hamburg, Goldschmieden, and Warsaw. In 1871, however, the price of soda suddenly fell, in consequence of the introduction of the ammonia-soda process, and the firm would have been in a very precarious position but for the by-product fluorspar, which in the meantime had come into very great demand for the manufacture of glass bottles. Simultaneously, important improvements took place in the alum industry, and foreign firms quickly ceased to manufacture soda from cryolite, only a few in America continuing to work Thomsen's method for a short time longer.

Cryolite also found use in the preparation of opaline glass, to which 10 per cent. was added. About 1890 began the preparation of cryolite enamels, these consisting of cryolite, felspar, quartz, soda, saltpetre, borax, etc. At the same time, Héroult discovered the new method for preparing aluminium, in which an electric current was passed through a bath containing fused cryolite and alumina in the proportion of 1 : 3. Cryolite contains only 12 per cent. Al, and for the preparation of 10 kg. Al about 80 times the quantity of cryolite is used. The latter only serves as flux in this case, since the raw material itself is alumina, which is an aluminium oxide with 53 per cent. Al, prepared from bauxite (an hydrated alumina). At the present time cryolite finds its greatest field in the enamel industry (for further details see end of chapter), to a secondary extent for the aluminium industry, and thirdly, for opaline glass. The cryolite deposits of Ivigtut extend 170 m. long and 60 m. wide, and have been mined 30 m. deep, while borings to 50 m. and further still showed the presence of cryolite. The winning process is similar to that of quarrying, although only hammers are used for chipping the mineral away ; the raw material is then shipped to Copenhagen, and from thence brought to the works. Here it is deposited on boards and well protected, so that dust and rain cannot deteriorate the pure white colour. The very large pieces are next broken up by hand hammers, and the cryolite classified according to

three sizes,—viz., up to 11, 22, and over, millimetres. The last two sizes are then purified from sand, three brands being recognised—pure white pieces, sold as lump cryolite; pure reddish pieces, which are pulverised; and a residue, which still contains other minerals. The residue from hand-sorting and sieving the raw cryolite is separated into four sizes—viz., meal with grains under 1 mm., the two next up to 14 mm. are purified by air blast, and when mixed together are termed grit. The coarser samples are broken up in special machines, which give little meal, and then pass with the raw material to the sieve. Meal and grit are treated differentially in settling tanks with a current of water, and then after an air separation are passed along to an electro-magnetic separation machine.

In this way cryolite is completely purified from admixture with other minerals, such as spathic iron ore, zinc blende, copper pyrites, iron pyrites, and galena glance. The quartz content is reduced to 0·2 per cent. in the cryolite used for aluminium manufacture, since a greater quartz content is injurious owing to the separation of silicon by the electrical process, which makes the aluminium brittle. The cryolite employed in the glass and enamel manufacture may contain several per cent. of quartz, since this is also present as a constituent.* Pulverised cryolite is a snow-white product, which may contain 0·1 per cent. Fe, but only an extremely small amount of Cu, Zn, or Pb. Cryolite is also sold in lumps as well as pulverised, and as such is disposed of to customers anxious to avoid possible adulterations in the powder, or, for export to countries where the tax on fragments is smaller.†

Natural cryolite does not possess to-day the same importance for the enamel industry as earlier, in spite of Jarl's opinion, owing to substitutes now being frequently used (artificial cryolite, sodium silicofluoride). Some chemical firms have achieved very good results with these, and prepare a relatively cheap product, which approaches natural cryolite in chemical composition, without possessing the impurities which the latter often contains.

Natural Greenland cryolite usually has only 93 to 94 per cent. of sodium-aluminium fluoride, the residue being mostly silica, which proceeds from the gangue of the mining operations.

* The author cannot confirm this assumption without further information.

† *Ingenioren*, 1909, vol. x., pp. 75-80.

Artificial Cryolite.—This compound, having the formula of sodium-aluminium fluoride ($3NaF . AlF_3$), is prepared by precipitating it with common salt when hydrated alumina is dissolved in hydrofluoric acid. This precipitated artificial cryolite contains more or less quartz, according to the purity of the raw material, and especially according to the content of hydrofluoric acid in the hydrofluosilicic acid.

The analysis of a pure artificial cryolite approximating in chemical composition to the purest natural cryolite gave :—

I.	Aluminium, . . .	13·25 per cent.
	Sodium, ...	31·30 ,,
	Fluorine, ...	53·90 ,,
	Calcium, ...	1·00 ,,
	Loss on heating, . .	0·60 ,,

Natural Greenland cryolite should consist of—

II.	Aluminium, . . .	12·85 per cent.
	Sodium, ...	32·85 ,,
	Fluorine, ...	54·28 ,,

(theoretical composition of natural cryolite) ; but this, however, contains almost always 6 per cent. impurity, especially of silica, and its actual composition is as follows :—

III.	Aluminium, . .	12·07-12·99 per cent.
	Sodium, . . .	30·88-32·30 ,,
	Fluorine, . . .	51·02-52·50 ,,
	Silica, etc., . .	1·00- 4·00 ,,
	Iron, . . .	0·00- 0·30 ,,
	Water, . . .	0·00- 0·27 ,,

Accordingly, pure artificial cryolite, as prepared by some chemical firms, approaches much more nearly in composition to the ideal cryolite formula than is the case with the usually contaminated Greenland samples.

A second analysis of an artificial cryolite gave :—

Aluminium, . . .	13·80 per cent.
Fluorine, ...	47·00 ,,
Sodium, ...	29·50 ,,
Silica, ...	2·00 ,,
Sodium carbonate, . .	4·00 ,,
Loss on heating, . .	3·70 ,,

Traces of chlorine and sulphuric acid;

Cryolite substitutes other than artificial cyrolites, which are mixtures of cryolite with fluorspar, sodium silicofluoride, felspar, etc., come on the market under various fantastic names. A preparation, which has been boomed for this purpose, was found to contain 12 per cent. zinc oxide.

A series of processes exist by which these are prepared, but only one or two may be discussed here. G. Loesekann.* has patented a process (D. R. P., 20th Nov., 1907), for preparing a pure cryolite from impure fluorspar alone. He heats fluorspar to redness with potassium sulphate and charcoal, extracts with water the mass obtained, decomposes this potassium-fluoride (KF) solution with sodium sulphate, and treats the resulting precipitate of sodium fluoride with aluminium sulphate [$Al_2(SO_4)_3$], whereby sodium-aluminium fluoride—*i.e.*, cryolite—is precipitated with regeneration of the sodium sulphate. The original solution also, containing potassium fluoride, may be treated with aluminium sulphate, whereby potassium-aluminium fluoride is produced.

To the author the result of employing this cryolite is unknown. At all events, every trace of sulphate must be removed from a cryolite so prepared, in order that it may be used with confidence for manufacturing enamels.

Sodium Silicofluoride.—In recent years this salt has been produced in large quantities during the manufacture of artificial manure (superphosphate), and placed on the market as a substitute for cryolite.

The following may be said regarding the manufacture of this product :—

Calcium superphosphate [$CaH_4(PO_4)_2$], or, as it is termed, soluble acid calcium phosphate is obtained by heating normal calcium phosphate (known as the mineral phosphorite) with sulphuric acid. The reaction proceeds according to the equation—

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4.$$

Naturally occurring phosphorite always contains impurities, such as calcium carbonate, and also fluorspar (CaF_2).

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

In addition, natural phosphorite contains admixtures of quartz and silicates, and the hydrofluoric acid arising from the

* *Chem. Ztg.*

fluorspar forms with these an evolution of gaseous silicon fluoride (SiF_4).

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

The above is a colourless, strongly-fuming gas with a powerful, obnoxious odour, which, when conducted into water, forms hydrofluosilicic acid (H_2SiF_6) and silicic acid (H_4SiO_4).

$$3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6.$$

It is possible also that the gelatinous silicic acid will be partly decomposed by the hydrofluoric acid present into hydrofluosilicic acid.

The solution of the H_2SiF_6 must now be separated from the insoluble silicic acid, an operation accomplished by the addition of common salt or soda, whereby sodium silicofluoride is thrown out as a white precipitate.

$$H_2SiF_6 + 2NaCl = \underset{\text{sodium silicofluoride}}{Na_2SiF_6} + 2HCl.$$

Many firms precipitate by means of cheap common salt, but enamelling practice has shown, however, that a better and purer product is prepared by precipitating with soda, since this is free from chlorides, which act so injuriously upon enamels.

From the nature of the manufacture above described, it is clear that the quality of the sodium silicofluoride coming on the market can fluctuate. By careless working the product can contain an appreciable amount of undesirable and worthless silica. The testing of sodium silicofluoride, therefore, includes the determination of the total sodium-silicofluoride content (which should not be less than 98 per cent.), and also the chlorine (which acts injuriously, and is present owing to precipitation by common salt instead of soda).

Formerly, these useless and injurious gases were allowed to pass into the air until the superphosphate firms were compelled by legislation to compensate the inhabitants and agriculturalists of the surrounding district, for it is clear that hydrofluoric acid gas evolved in large quantities will act injuriously upon plants, as also upon the respiratory organs.

Under the pressure of strict factory legislation and of continual complaints, the firms have endeavoured to intercept these obnoxious gases and turn them to account. Only about half of the evolved

gas can be regained as sodium fluosilicate, however, while a part is retained mechanically by the superphosphate as silicon tetrafluoride, SiF_4, or as hydrofluosilicic acid, H_2SiF_6. A fraction of the fluorspar contained in the phosphorite is in general not decomposed by sulphuric acid. In spite of the high cost entailed by a plant for intercepting the hydrofluoric acid gas and converting it into sodium silicofluoride, there are scarcely any superphosphate firms to-day which allow the gases to escape. The price obtained for the sodium silicofluoride amply covers the cost, however, and generally adds to the profit (20s. to 30s. per 100 kg.). For a marketable ware the sodium silicofluoride must be at least 98 per cent. pure, white, and finely powdered.

The technical production consists in conducting the fluorine gases, and silicon fluoride in particular, into water, filtering the hydrofluosilicic acid through filter presses into vats made of pitch-pine wood (since wood is least attacked), and precipitating the sodium silicofluoride by soda; the upper liquid is then drawn off, and the precipitate well washed, dried in kilns, and finely ground. Chemical firms are said to make 30 to 50 per cent.* on the product after defraying the cost of building and expert advice.†

Recently other processes have been patented for the preparation of this product, though these can scarcely compete with that obtained as a by-product in the manufacture of superphosphate. That of the Rützerwerke A.-G. Berlin (D. R. P. 188,651, of 2nd Oct., 1906), consists in making an addition of material containing a large amount of fluorine and silica, while using the absorption plant in the superphosphate works for working up the crude phosphate, and at the same time obtaining valuable manure. In expert circles this process has been condemned, since such fluoride additions are said to be deleterious by increasing the sodium-silicofluoride production at the expense of a lower grade and less valuable superphosphate. The material proposed for addition is potash felspar.

Artificial Cryolite.—The following examples of the composition of some cryolites show how much the composition of an artificial cryolite can vary, and how important it is that only a reliable firm should be patronised for the purchase of this material.

* These data appear to be much exaggerated.

† *Chem. Ztg.*, No. 63 (1909), p. 563.

I. An artificial cryolite* contained—

95 per cent. sodium-aluminium fluoride ($3NaF \cdot Al_2O_3$),
5 per cent. silica (SiO_2).

This is a fairly good product, corresponding almost entirely to the purest natural cryolite. No matter where purchased, 5 per cent. of less valuable quartz must be allowed for on mixing.

2. Another artificial sample contained—

80 per cent. sodium-aluminium fluoride,
20 per cent. almost valueless quartz.

This was naturally cheaper and, therefore, of inferior quality. Many enamel firms not managed by experts are often deceived by the abnormally cheap price when purchasing these products. In this case it is certainly not the cryolite vendor who is to blame.

3. The following artificial cryolite showed a still more interesting composition :—

18 per cent. aluminium fluoride (AlF_3),
50 per cent. sodium fluoride (NaF),
32 per cent. silica (SiO_2).

4. A fourth sample contained—

26 per cent. AlF_3,
40 per cent. NaF,
32 per cent. SiO_2.

The possible variations and causes of failure in enamel preparation will readily be gathered from these examples. Artificial cryolite, however, must not be condemned entirely, since a product with compositions corresponding to No. 1 above may certainly be substituted for natural cryolite, especially as it is usually cheaper than the latter. As a rule, I*a*. artificial cryolite is almost entirely silica free. The analysis of such a cryolite gave the following satisfactory composition :—

Aluminium,	13·30	per cent.
Sodium,	32·50	,,
Fluorine,	52·20	,,
Iron,	0·02	,,
Silica,	1·00	,,
Water,	0·98	,,

* Grünwald, *Theory and Practice of Enamelling on Iron and Steel.* C. Griffin & Co., London.

Guarantees as to the composition should be required on purchase, especially with regard to the silica content, for which frequent analyses should be made. The injurious effect of a cryolite containing 32 per cent. quartz in an enamel preparation need hardly be emphasized. The unsuspicious enameller who is incapable of calculating the composition of his mixed raw products appreciably increases the silica content of his enamel, and thereby acquires an insufficiently opaque result of fluctuating composition.

Melting Point of Cryolite.—The melting points of mixtures of cryolite and aluminium oxide (Pyne and Hardcastle, *Sprechsaal*, 1907, No. 2).

Cryolite, .	100%	97%	96%	95%	94%	93%	92%	90%	85%	80%
Aluminium oxide,	0%	3%	4%	5%	6%	7%	8%	10%	15%	20%
Melting point,	1,000°	974°	960°	915°	960°	982°	992°	980°	994°	1,015°

The Rôle of Cryolite and of Fluorine Compounds generally in the Enamel.—Cryolite plays a double rôle of great interest in enamel manufacture, since it acts as a flux, and at the same time is an agent for producing opaque enamels, although the latter opacity-producing property is limited and by no means equal to that of tin oxide. The latter, however, is correspondingly more expensive.

Much has already been recorded concerning the peculiarity of fluorides in lowering the melting point. While lime (CaO) alone may scarcely be regarded as an aid to melting, calcium fluoride—*i.e.*, fluorspar (CaF_2) is readily fusible, and the influence of the fluorine rendered evident.

Cryolite at its melting point combines in part with the silica of the enamel to form a sodium-aluminium silicate, while part volatilises as silicon fluoride (SiF_4). The opinion expressed in certain quarters * that in general the total fluorine content is evolved as silicon fluoride must by all means be confirmed. According to Erik Encquist,† the turbidity is produced by the fluorine gases enclosed in the fused glass or enamel on cooling,

* Bock, "Bedeutung des Fluorin Emailgläsern," *Chem. Ztg.*, 1908, pp. 730 and 893.

† *Chem. Engineer*, 1909, vol. x., p. 54.

should there have been no overheating on melting. This, however, is only a theoretical speculation.

Beurath * traces the white turbid action of the cryolite to the separation of excess alumina which is not dissolved by fused fluorine compounds, such as sodium fluoride, but remains finely divided therein, and on cooling occasions the turbidity.

Karl Riedel,† of Reinowitz, takes exception to Encquist's proposals, and expresses the opinion that the sodium fluoride content of the cryolite has no influence whatever on the turbidity of the glass, since the fluorine is expelled as silicon fluoride. He draws these conclusions from the following fusion experiments :—‡

(1) An opaline glass with the corresponding amount of aluminium hydroxide was introduced in place of cryolite, and gave no turbidity, but a crystal clear glass ; therefore, the alumina content of the cryolite cannot be the sole cause of turbidity.

(2) A glass mixture in which the cryolite was replaced by the equivalent amount of sodium fluoride gave an opalescent turbid glass if the fusion was not carried out at too high a temperature. The turbidity, however, was less intense than that produced by cryolite.

(3) The addition of fluorspar in not too small amounts gives an opalescent glass in the absence of any other opaquing agents.

From these results Riedel believes it to be established that the sodium-fluoride content of the cryolite, or an addition of fluorspar, contributes to the turbidity of the glass ; it remains for investigation whether the turbidity can be produced by the compounds themselves, or by reaction products, or even by union of the fluorine with the alumina of the melting pots.

Reasoning from the above results, Riedel offers some remarks, in which he does not deny the possibility of glass and enamel being rendered turbid by a gas ; he shows, however, from a series of experiments in which a gas is with certainty excluded as a means of producing opacity—*e.g.*, by the addition of 6 to 10 per cent. bone ash to a glass mixture proper—that a crystal clear glass was obtained which only became opalescent by repeated heatings and coolings. With larger phosphate additions the glass is clear when hot, but turns milky-white on cooling. Also, by the introduction of arsenic, saltpetre, and red lead to a glass

* " Ueber Kryolithglas," *Die Gl. Pol. J.*, vol. cxcii. (1869), p. 239.

† *Chem. Ztg.*, 1909, No. 149, p. 1305.

‡ Abstract from *Sprechsaal*, No. 2, 1910, p. 27.

mixture, turbidity was produced on cooling, which must here be assumed as due to an arsenic compound, and not to a gas. This glass, however, exhibits the property of losing its ability to become turbid if the heating be too severe, although this might be traced to decomposition reactions of the arsenates.

In conclusion, Riedel notes the behaviour of gold and ruby-copper glass, also glass coloured by cadmium sulphide, which by alternate heatings and coolings assumes a beautiful greenish-yellow colour.

Whether fluorine is present in the fused enamel or not might depend, in the first place, on the temperature of the melting furnace and the duration of fusion. We must on analytical grounds assume that in most cryolite- or fluorspar-containing enamels fluorides are still present, in view of the relatively moderate fusion temperatures. Only by prolonged fusion and at high temperatures can the case arise where the total fluorine in the enamel is expelled as silicon fluoride, and this only when sufficient silica is present for the decomposition. The injurious influence upon vegetation of the fluorine gases expelled from the melting furnace, which Bock asserts have occurred, could never be confirmed by the author in the case of the largest of European enamel works, which melted over 12,000 kg. enamel daily. Whether fluorine really influences the turbidity has not as yet been confirmed.

Many tokens, however, point to the contrary, and the turbid action is generally traced to a separation of insoluble matter. By many people precipitated silica is regarded as the turbidity agent. Soda-lime glasses very rich in silica become turbid on cooling without any addition.

A patent by Lesmüller (D. R. P., 218,316, of 1st April, 1909), makes use of the property that on melting together borax or boron trioxide with the oxides of quadrivalent elements, such as silicon, tin, lead, titanium, zirconium, or thorium, only colourless glasses arise when sufficient fusion material is at hand. The solution ensues much more readily when silica is present with the above-named products. In such fused melts of these boric acid glasses saturated with the above tetravalent oxides, turbidity ensues on cooling in a current of steam or acid vapour, which is due to the separation of particular double compounds of boric acid. These substances separate on prolonged cooling as extremely fine amorphous masses, and are distributed uniformly throughout

the glass flux. Such complex boron compounds are very permanent towards acids and alkalies, being only brought into solution by hydrofluoric acid. For the preparation of such glazes, the boric acid compound is melted with one or more of the oxides named in such proportions that a melt saturated with the oxide arises, while during cooling a current of steam or acid vapour is led over or through the flux, and the product obtained then added to the glass or enamel mixture.

Several communications on the rôle of fluorine in enamel glazes take up a contrary standpoint, and these will now receive attention. Bock * favours an artificial cryolite of correct composition. In order to separate artificial cryolite from valueless admixtures, he proposes to submit a sample to prolonged vigorous boiling with a large excess of distilled water, and filter off the residue (alumina and silica), precipitating the dissolved sodium silicofluoride with boiling barium-chloride solution.

$$Na_2SiF_6 + BaCl_2 = BaSiF_6 + 2NaCl.$$

The slightly rainbow-coloured insoluble precipitate of barium silicofluoride should be a certain proof that one has to deal with a mechanical mixture of sodium silicofluoride and other substances.

Bock is of opinion that fluorine itself possesses a subordinate influence upon glass turbidity, and only produces a lowering of the melting point in the form of its salts. He assumes that all the fluorine volatilises on fusion as silicon fluoride, the sodium silicofluoride decomposing as follows :—

$$2Na_2SiF_6 + SiO_2 = 3SiF_4 + 2Na_2O.$$

The presence of silica or silicates is naturally a fundamental necessity. The same degree of turbidity will be obtained by the addition of pure alumina, soda, etc., inasmuch as the resulting glass, as regards its separate components, is quantitatively equal or closely approximates to a glass prepared from cryolite. At the conclusion of his work, Bock utters a warning with respect to the injury caused by fluorine gases expelled from enamel works, although, as already mentioned, the author could never confirm such action. The idea of utilising the fluorine gases expelled from the enamel melting furnaces by transformation into sodium silicofluoride, as in superphosphate works, has not as yet materialised in any enamelling firms.

* *Chem. Ztg.*, 1908 (62), p. 730.

Meyer and Havas,* in an interesting communication, have contested this opinion of Bock. Both authors, however, make the erroneous assertion that fluorspar melts at 900°, while, according to the observations of Ruff and Plato, this only happens at 1,400°. Meyer and Havas give two examples to illustrate, not only that the turbidity effect of cryolite is appreciable, but that only a part of the fluorine is lost during the melting process when the operation is not too prolonged. They analysed two ground and two cover enamels, finding :—

	Ground Enamel I.		Ground Enamel II.		Cover Enamel.		
	Composition.		Composition.		Composition.		
	Calculated.	Found.	Calculated.	Found.	Calculated.	Found.	
	Per cent	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
SiO_2,	50·48	51	65·02	64·86	55·86	55·91	SiO_2
B_2O_3,	16·34	15·79	9·70	9·46	7·48	6·96	B_2O_3
CaF_2,	6·81	5·44	4·83	3·67	4·48	3·95	Al_2F_6
CoO,	0·27	0·25	0·20	0·21	6·85	6·03	NaF
MgO,	0·67	0·71	0·49	0·51	1·96	1·73	CaF_2
Al_2O_3,	7·75	7·86	6·23	6·45	9·59	10·30	Al_2O_3
CaO,	0·23	1·51	0·17	1·01	0·36	0·54	CaO
K_2O,	2·38	2·60	1·65	1·71	1·66	1·73	K_2O
Na_2O,	15·07	14·84	11·71	12·12	11·76	12·85	Na_2O

By comparing the calculated composition from the mixed raw materials with that found by analysis, a fluorine loss on fusion of 20·2 per cent. was established, while the fluctuation of the silica content had no appreciable influence on this fluorine loss. With the cover enamel, which contains cryolite in addition to fluorspar, the fluorine loss was only 11·85 per cent. This supports the fact that cryolite gives off fluorine by interaction with the enamel components with greater difficulty than fluorspar at the fusion temperature of the enamel.

Vondracek † assumes it as a certainty that the aluminium fluoride is the turbidity factor, and illustrates the melting operation schematically by the following equation :—

$$4Na_3AlF_6 + nSiO_2 = 6Na_2O, (n - 3)SiO_2 + AlF_3 + 3SiF_4.$$

Sheet enamels require a large expansion capacity when

* *Chem. Ztg.*, 1909, Nos. 83 and 84, p. 758.

† *Sprechsaal*, No. 40 (1909), p. 589, and No. 42 (1909), p. 584.

warmed, which is attained by an increased cryolite addition. The extreme limit for the latter addition to enamels is given by Vondracek as about 15 per cent. For cast-iron enamels, however, an addition of only 5 per cent. cryolite is admissible, as otherwise, hair-like cracking of the enamel is alleged to take place, although the author has never confirmed this assertion. A higher cryolite content with a lower one of felspar favours crack formation.

The problem as to whether the fluorine in the enamel remains behind or is entirely expelled during fusion has been the subject of numerous, often contradictory, investigations. G. Vogt,* the director of the famous French porcelain works at Sèvres, has made a report on the influence of fluorine in refractory fire glazes.

Of soda and lime containing pegmatite there are usually					76·5 parts.
Of kaolin	,,	,,	,,	,,	1·3 ,,
Of quartz sand	,,	,,	,,	,,	12·0 ,,
Of fluorspar	,,	,,	,,	,,	11·3 ,,

The glaze was perfectly vitreous and transparent after firing upon platinum foil in the oxidising flame at 1,300° C. Vogt analysed the unfused raw mixture, as well as the fused glaze, in order to determine the silica, alumina, lime, and fluorine (the latter by the standard method of Berzelius), and found :—

	Raw Mixture.	Fused Product.
SiO_2,	68·22 per cent.	70·84 per cent.
Al_2O_3,	13·89 ,,	14·12 ,,
CaO,	3·06 ,,	10·41 ,,
Ca, F, 9·56	4·91 ,,	..
	4·65 ,,	..
Alkali as difference,	5·27 ,,	4·63 ,,
	100·00 ,,	100·00 ,,

From the analysis of the fused product it was found that all the fluorine had disappeared, according to the equation—

$$SiO_2 + 2CaF_2 = SiF_4 + 2CaO.$$

Naturally this presumes a sufficient quantity of silica present for conversion of the fluorine into volatile silicon fluoride. Nevertheless, Vogt admits that glazes prepared with fluorspar possess greater lustre after firing, while the colour of the pigments added is better developed than in a glaze prepared without fluorspar.

* VI. Int. Congress of Applied Chemistry, London, 27th May to 2nd June, 1909. See *Sprechsaal*, No. 23, p. 346, 1909.

We have to thank R. Vondracek* also for the interesting research into the fluorine problem, which has been earlier discussed.

The following conclusions may perhaps be drawn from a survey of all these investigations :—

(1) Fluorine appears to be expelled from fused enamel as silicon tetrafluoride only under certain conditions—viz., at very high temperatures, with prolonged fusion, and in the presence of sufficient silica.

(2) At the usual temperatures of enamel fusion a smaller or larger proportion of the fluorine content of the added fluorspar, cryolite, sodium silicofluoride, etc., remains bound up in the enamel, possibly in an occluded state.

(3) Fluorspar loses its fluorine more readily from enamels than cryolite, in spite of the fact that the former melts at 1,400° C., and the latter even at 1,000° C.

The fluorine appears to be more loosely bound to the calcium (*i.e.*, to possess smaller affinity) than to sodium and aluminium.

Concerning the enamel manufacture in particular, practical experience has yielded the following facts :—

(1) In the manufacture of blue enamel natural cryolite is preferable to similar substitutes, since the latter do not possess exactly the same composition as the natural variety.

(2) Sodium silicofluoride produces a lower turbid effect, and is of less value for lowering the melting point and enhancing the lustre, than natural cryolite or an artificial cryolite substitute of analogous composition.

(3) For ground enamels the addition of cryolite is, as a rule, avoided, since on the one hand, no turbidity is necessary, and on the other, such ground enamels easily foam and blister on firing.

(4) In general only the best brands of cryolite should be employed, and as the natural varieties are not always quite pure, but contain silica, many first-class qualities of artificial cryolite, having the exact composition $3NaF \cdot AlF_3$ with no silica content, are to be preferred to these natural cryolites.

(5) Natural cryolite should only be obtained in lumps, so as to be certain of purchasing a pure first-class product.

(6) The turbidity effect of all fluorine compounds is limited in degree, and never attains that of tin oxide.

* *Sprechsaal*, No. 40 (1909), p. 585.

Other examples * of cryolite substitutes to be found in the literature are as follows :—

A mixture of fluorspar and felspar (spar glass) is recommended in an American patent by Toping (663,618), but the value of such a substitute is questionable.

Tedesco (D. R. P., 31,112) recommends normal or acid alkaline fluorides (D. R. P., 33,425). In both cases the presence of aluminium compounds is assumed.

R. F. Wagner (D. R. P., 196,897) proposes artificial aluminium fluoride. Schwarz † asserts that zinc fluoride can also produce turbidity in glass, and he gives an example of a spar glass in which alumina is completely absent :—

SiO_2,	67·80 per cent.	MgO,	1·22 per cent.
Fe_2O_3,	0·28 ,,	Na_2O,	9·05 ,,
ZnO,	9·20 ,,	K_2O,	0·23 ,,
CaO,	8·00 ,,	F,	3·54 ,,

L. Petrik ‡ has obtained opaque zinc glazes containing boric acid, but no fluorine, without being able to explain in what form zinc oxide possesses this property.

Alumina, also, is an opacity agent under certain circumstances (and in many quarters is regarded as the cause of this property in cryolite), while it dissolves less readily in lead glazes than in those where lead is absent.

Hock obtained a good opaline glass by melting together 100 parts of felspar with 22 parts of red lead—*i.e.*, with no fluorine. He has recently shown that for enamel preparations felspar is to be preferred to quartz.

Kempner (D.R.P. 61,777 and 165,986) proposes alkaline silicofluorides as opaquing agents.

Finally, a recent patent by Humann and Teisler, of Dohna, may be mentioned, of which the following is an abstract :—

Preparation of Aluminium-Sodium Fluoride—Humann and Teisler.—This compound is prepared in the known way by the action between molecular proportions of alumina, soda, and hydrofluoric acid, whereby the double salt separates in sparingly soluble form. It has now been established that sodium silicofluoride is more advantageously employed in place of the hydro-

* Quoted from the earlier mentioned work of Vondracek.

† *Verhldn. z. Bef. d. Gewerbefl.*, 1877, p. 117.

‡ *d. Tonwarenindustrie*, 1908, pp. 20, 68, 74.

fluoric acid. It is true that the product obtained contains silica finely distributed therein, but it is entirely suitable for ceramic purposes. The reaction takes place in the sense of the equation :—

$$2Na_2SiF_6 + Al_2O_3 + Na_2CO_3 = Al_2F_6 + 6NaF + CO_2 + SiO_2,$$

and goes best to completion in the presence of water and by the use of materials as finely powdered as possible (French patent, 408,134, Oct. 20th, 1909).

Some recent patents dealing with the production of artificial cryolite will now be communicated from reports in the *Chem. Ztg.**

The apparatus which serves for the preparation of sodium

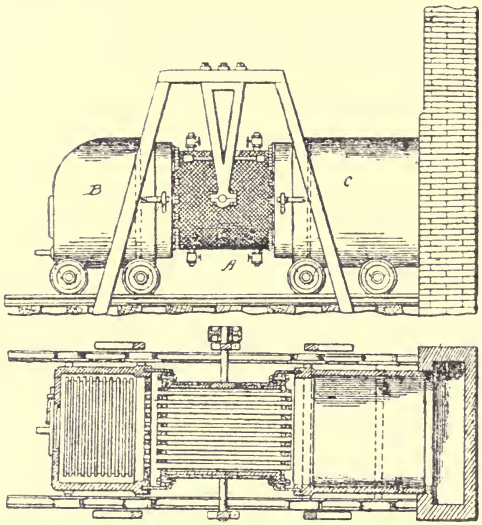


Fig. 5.—Apparatus for Preparation of Sodium Aluminate.

aluminate, as well as for other sodium-aluminium compounds (see also the following abstract) consists of the retort A (Fig. 5), the furnace B, and the cylinder C, which connects the retort with the chimney. The retort may be secured by suitable locks to the furnace and cylinder C.

As soon as these locks are unfastened the retort remains suspended in a movable frame. The retort is lined with asbestos, is intersected by hot pipes, possesses four exit pipes provided with taps, and may be closed by doors. The furnace contains a

* *Chem. Rptorium.*, p. 291, 1910.

tube for charging the gaseous or liquid fuel, a grate, and a perforated plate upon the side next the retort whose apertures correspond to the heating pipes of the retort. The whole system is movable upon wheels, and fitted so that it may be transported either entire or in its separate sections. The cylinder C serves solely to expedite the passage of the fuel-combustion products into the chimney, after going through the heating pipes of the retort. For certain reactions with this apparatus the retort is lined inside with a uniform layer of gas carbon. This is done by filling the retort with coal, which is then submitted to distillation. The gas hereby evolved is conducted by the pipes possessing taps into special holders for further use, the coke being removed at the end of the operation. During the distillation the retort is often rotated in order to bring about a uniform distribution of the gas carbon in every part of the retort. Clay, bauxite, or corundum, serve as raw material for the preparation of sodium aluminate. Clay, for example, is heated with the corresponding amount of acid sodium sulphate, whereby silica, sodium sulphate, and a double compound of aluminium and sodium sulphates of formula $Al_2(SO_4)_3 . 3Na_2SO_4$ is produced. The reaction product is removed from the retort by steam or hot water, filtered from the insoluble silica, and the double sulphate obtained by evaporating the filtrate to dryness, is then heated in a carbon-lined retort. The compound $Al_2O_3 . 3Na_2S$ remains behind with evolution of sulphur dioxide (which is used for the preparation of sulphuric acid), carbon monoxide and dioxide, and is converted into the compounds sodium aluminate, $Al_2O_3 . 3Na_2O$, and calcium sulphide by a further heating with burnt lime. By treatment with water the sodium aluminate passes into solution, while the insoluble calcium sulphide remains behind (V. St. Amer. Pat., 957,848, of 10th May, 1910, submitted Sept. 29th, 1909).

The preparation of aluminium fluoride and other aluminium compounds may be carried out in the above-described apparatus. The double salt of aluminium and sodium sulphates obtained by heating clay with acid sodium sulphate is fused with cryolite, whereby aluminium fluoride and sodium sulphate arise, according to the equation :—

$$Al_2F_6 . 6NaF + Al_2(SO_4)_3 . 3Na_2SO_4 = 2Al_2F_6 + 6Na_2SO_4,$$

and may be separated by water extraction. From the dried aluminium fluoride artificial cryolite can be won together with

metallic aluminium, by the action of metallic sodium. The reaction proceeds according to the equation :—

$$2Al_2F_6 + 6Na = 2Al + Al_2F_6 . 6NaF.$$

Further, sodium sulphide is obtained by heating sodium sulphate in retorts lined with gas carbon, which, when heated to 800° with burnt lime in the same retort, yields metallic sodium according to the equation :—

$$6Na_2S + 6CaO + 6C = 6Na_2 + 6CaS + 6CO.$$

Finally, the solution of sodium aluminate (compare the previous report) can be converted into artificial cryolite by the action of hydrofluoric acid :—

$$Al_2O_3 . 3Na_2O + 12HF = Al_2F_6 . 6NaF + 6H_2O.$$

(V. St. Amer. Pat., 957,754, of May 10th, 1910, submitted May 29th, 1909).

VII. PYROLUSITE (MnO_2).

Manganese dioxide is found in huge deposits as polianite and pyrolusite, both of which are identical in chemical constitution, polianite, however, having a different state of cohesion than the softer pyrolusite. Polianite is found in the Erzgebirge, Schneeberg, Johanngeorgenstadt, Nassau, and Cornwall.

Pyrolusite forms short prisms vertically striated; sometimes it occurs in isolated fibrous forms, or in small tables; also in grape-like, kidney-like, shrub, and bud-like aggregates of radial stem and fibrous structure, or again in compact and earthy varieties. The hardness is very low—viz., 2 to 2·5—while it may be even softer. It is dark steely-grey to light iron-black in colour, leaves a streak, and possesses a feeble semi-metallic or silky lustre in the fibrous varieties.

Technically, pyrolusite is manganese peroxide, MnO_2, often possessing a small water content.

Pyrolusite is regarded as a derived product of manganite (manganese hydroxide, $Mn_2O_3 . H_2O$). The transformation ensues by the exchange of water for oxygen. Pyrolusite may, however, be formed naturally from manganese spar ($MnCO_3$), and also by the weathering of chalylite and limonite containing manganese. Pyrolusite is found at Johanngeorgenstadt, Raschau, Platten, Arzberg, Horhausen, Lindener Mark in Nassau, Eiserfeld, Ilfeld, Ilmenau (Thuringia), Elgerburg, Macska-Mezö in Hungary, Romanêche in France, Vermont.

Recently large deposits have been exposed in Japan at Hokkaido, Aomori-Kew, Kioto-Fou, Oroani (Prov. Mitau), and, in the year 1907, 65,000 dollars' worth of pyrolusite was exported from this source.

The mineral is also found in stratified deposits with oolitic structure in the Caucasus, while as pelagite it is brought up in nodules from the Pacific Ocean floor.

The following details concerning the occurrence and extent

of the most important manganese minerals are taken from a work by Haenig.*

The export of pyrolusite from the Caucasus suffered a decline during the last political trouble in Russia, and other sources had to be sought.

Concerning the use of manganese-containing ores, one speaks of poor or industrial manganese ores (for the preparation of ferro-manganese and spiegel iron), and rich ores—*e.g.*, pyrolusite —which alone deserve attention from our standpoint.

The pyrolusite occurring in nature never corresponds exactly to the formula MnO_2, but contains mineral admixtures. For example, the complete analysis of a Caucasian pyrolusite gave the following composition :—

MnO (manganous oxide),	—
Mn_2O_3 (manganese sesquioxide),	1·54 per cent.
MnO_2 (pyrolusite or manganese peroxide),	84·86 ,,
SO_3 (sulphuric anhydride),	0·40 ,,
FeO (ferrous oxide),	0·79 ,,
PbO (lead oxide, plumbous oxide),	0·18 ,,
CuO (cupric oxide),	traces
Al_2O_3 (alumina),	1·80 ,,
P_2O_5 (phosphoric anhydride),	0·36 ,,
CaO (lime),	0·43 ,,
MgO (magnesia),	0·27 ,,
BaO (baryta),	1·58 ,,
Alkali,	0·41 ,,
SiO_2 (silica),	5·09 ,,
CO_2 (carbon dioxide),	0·34 ,,
H_2O (water),	1·95 ,,

Many varieties of pyrolusite contain cobalt, zinc, and arsenic. Localities in Europe are :—

Germany.—Near Coblentz at Dr. Geyer's Works, Amalienhöhe and Elisenhöhe, in Waldagesheim ; also the Konkordia and Schloszberg pit at Seibersbach.

In Hesse at Ober- and Niederroszbach, near Weilburgh (Bonn) ; also at Obertiefenbach in North Thuringia. In the year 1905 the German production amounted to 51,000 tons, of approximate

* A. Haenig, *Jahrb. der kk. montanist. Hochschulen*, vol. ii. (1909).

value 700,000 francs, yet this yield of ores rich in manganese was insufficient to meet the demand.

France.—Romanêche (Psilomelane). Pyrolusite must be imported.

Austria-Hungary.—Bohemia, Upper Austria, Steiermark, Bukowina, Kärnthen, Krain. In 1907 there were only two iron works. The Teresia pits (Arsita-Ken) in Bukowina deliver a mixture of manganese silicate and pyrolusite, which, after sorting and washing, yields a pyrolusite of 65 to 72 per cent. MnO_2.

The total production in Austria-Hungary is about 100,000 tons, and this country counts among the principal sources. Hungary is poor in manganese ores.

Russia.—(*a*) Caucasus—In the Valley of Tschiatura pyrolusite forms stratified beds 120 km. long, whose total bulk is estimated at 90,000,000 tons. In spite of the prodigality and abuse of those having guaranteed concessions, the winning of pyrolusite is certain for years to come. One-third of the production passes *via* Poti and Batum to England, a similar amount to Germany, and the remainder to America, Russia, etc.

In the province of Jekaterinnoslaw, deposits occur at Nikofol with 20,000 hectares surface, having an average content of 45 per cent. Mn. The total amount of pyrolusite is estimated at 33,000,000 tons.

Demaret-Fresen * report an important source at Jvanorka and Horodisce on the River Tomakovka. The deposits have a depth of 1 to 4 m. (on the average 2½ m.), are bedded horizontally, and consist of granular pyrolusite which is easily separated from the adherent clayey sand. The mining is subterranean and simple. The mineral is washed in drums, and consists of :—

50 per cent. MnO_2 (pyrolusite),

8 per cent. silica,

Traces of phosphorus,

The difference is earthy matters and clay.

Spain.—The annual production of manganese ores is 63,000 tons.

* "Les Champs de Manganèse de la Tomakovka," in *Echo de l'Industrie*, 28th Oct., 1902.

Turkey.—Numerous, but almost unexplored, sources exist in Asia Minor, on the coast of the Sea of Marmora, and near Smyrna. In Cassandra 60,000 tons are annually produced, containing—

44·83 per cent. Mn,
2·45 per cent. Fe,
9·40 per cent. SiO_2,
5·18 per cent. CaO.

In the future these sources may play an important part. In Cape Colony (Paarl), New South Wales, and Queensland (Mount Miller) ores occur with 79 per cent. of pyrolusite.

In the *United States* there are numerous sources in California, Georgia, Tennessee, Virginia, Arkansas, and West Texas, while the Island of Cuba is rich in manganese ores.

Brazil.—Over 192,000 tons annually are produced at Minas-Geraes in Brazil.

In the Straits Settlements the deposits of pyrolusite are very considerable, and, according to estimates, a single district could annually produce 1,306,782 tons. The deposit is much thicker than in the Caucasus, and is estimated at 10,000,000 tons. Unfortunately, the pits are at fairly high altitudes, and often accessible only with difficulty, while the expensive and casual labour, together with the unsound climate, retard extensive operations.

India.—Rich deposits occur in India at Nagpur, Bhandara, Balaghat, Chindoara, Jabalpur, and in 1906 the yield of manganese ores exceeded 500,000 tons.

Japan, as previously mentioned, produced 10,000 tons in the same year.

The following are, therefore, the most important countries where manganese ores are mined :—

Russia,	producing	505,000	tons annually.
India,	,,	500,000	,,
Brazil,	,,	200,000	,,
Spain,	,,	68,000	,,

The total production is about 1,243,000 tons.

The following table gives analyses of the more important manganese ores :—

Table showing the Chemical Composition of Manganese Ores (according to Venator).

Country where found.	Mn.	Fe.	SiO_2.	P.	Al_2O_3	CaO.	CO_2.	S.	H_2O.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Bosnia—									
Celvijunovic, sorted,	46·01	5·30	12·38	0·07	2·76	..	..	0·94	..
Do., do.,	50·42	3·53	11·48	0·07	0·90	..	..	..	..
Brazil—									
Miguel Burnier,	55·00	..	1·50	0·03	..	..	..	..	..
Carlos Wigg, .	44·43	2·99	0·94	0·03	2·26	0·54	..	..	4·01
Aver. analysis,	54·08	0·90	1·05	0·03	..	..	..	..	..
From consignments to England, 1900,	53·35	..	1·02	0·03	..	..	..	..	15·81
Do. to North America, 1900,	53·46	..	1·11	0·03	..	..	..	..	13·00
Chili—Santiago,	53·00	..	..	0·05	..	1·13	..	0·02	..
Coquimbo,	52·66	..	..	0·06	..	2·33	..	0·05	..
France—									
Las Cabesses—									
Crude mineral,	40·92	1·75	6·50	0·04	..	6·00	..	..	..
Roasted do.,	50·56	2·00	8·50	0·05	..	7·00	..	..	..
St. Giron, .	45·68	..	5·94	0·43	..	..	..	..	..
Greece—									
Mils. average, .	34·73	3·00	22·92	0·06	..	2·15	..	..	..
Japan—No. 1, .	51·19	..	7·30	0·06	..	..	..	..	..
No. 2, .	44·09	..	16·10	0·06	..	..	..	..	..
No. 3, .	48·29	..	10·10	0·09	..	..	..	..	..
Russia—									
Caucasus—									
Max. content,	58·20	0·41	5·22	0·13	0·89	0·08	1·22	0·09	..
Min. do.,	45·50	..	7·38	0·48	..	..	..	..	5·78
Mean of 5 ores,	54·00	0·02	4·62	0·34	0·55	0·27	0·32	..	1·88
Jekaterinenburg,	53·70	0·86	8·10	trace	..	1·37	..	0·08	..
Spain—									
Huelva—									
Manganese—									
carbonate, 4,	28·26	6·58	4·95	..	2·11	..	..	..	..
carbonate, 6,	41·15	0·77	14·10	..	1·41	..	..	..	..
Santa Domingo,	38·87	1·37	22·50	..	1·80	..	..	..	..
Manganese carbonate,	38·33	2·31	10·85	0·10	0·35	2·87	29·88	..	1·54
Roasted mineral,	49·60	..	..	..	..	..	..	..	..
United States—									
Ark. Batesville—									
Pit 1, . .	56·92	..	2·10	0·10	..	..	..	..	..
Pit 2, . .	54·33	..	1·34	0·29	..	..	..	..	..
Keystone pit,	57·50	1·75	2·31	0·12	..	..	..	..	..
Martin pit, .	60·50	1·61	1·00	0·17	..	..	..	0·03	10·45
India—Gosalpur,	54·29	..	3·27	0·16	3·19	..	..	2·81	..
Average,	51·43	5·60	95·2	0·09	..	..	..	..	..

The Rôle of Pyrolusite in Enamel Manufacture.—Pyrolusite fused with enamel imparts to it a rose to blackish-violet colour when no reducing gases or substances are present; in the latter case the pyrolusite would be degraded to a lower degree of oxidation, and, therefore, possess inferior colouring properties. Saltpetre, for example, is added to the enamel to develop the manganese colour. For especially pure clays,* a pure manganese oxide is prepared by treating finely-powdered pyrolusite with hot hydrochloric acid, whereby a vigorous evolution of chlorine takes place, and when this has ceased the mixture is diluted with water and weak ammonia solution added. The dark brown precipitate formed is well washed, dried, and heated gradually with stirring until red hot; after this calcination the manganese oxide is finely powdered. It is more simply prepared from a solution of manganese vitriol (manganese sulphate) to which ammonia is added as long as a precipitate forms. This precipitate is filtered off, washed, dried, and heated to redness. The product so obtained is iron-free, and therefore purer than that prepared by the first method, since the pyrolusite frequently contains iron compounds, which are dissolved by treatment with hydrochloric acid and precipitated together with the manganese oxide during the addition of ammonia.

It is obvious that a manganese oxide contaminated by iron compounds would give a violet shade less pure than that afforded by an iron-free product.

For white enamels it is customary, for preventing any discolouration—viz., a yellowish colour, due to iron oxide present in small amounts in the raw materials—to add traces of cobalt oxide or pyrolusite to the enamel mixture. These operate so that the yellowish colour is corrected by the complimentary blue or violet-red respectively to a pure white. Only quite small amounts of pyrolusite must be added, however, for decolourising the raw enamel (about 20 to 50 grammes per 100 kg.).†

Since pyrolusite is used in relatively small amounts for enamelling purposes, only the best qualities should be procured. In blue enamels it is customary to mix 1 to 5 per cent. pyrolusite in addition to 1 per cent. cobalt oxide, in order to strengthen the dark blue effect of the more expensive cobalt oxide by the cheaper pyrolusite. Naturally this takes place with injury to the pure

* Hermann, *Die Glas-, Porzellan-, und Emailmalerei.*

† In this case pyrolusite is the oxidant of the organic impurities.

blue cobalt colour, which, by addition of pyrolusite to the enamel, is changed to a blue-violet shade, although the latter is often desirable on the market.

A moderate addition of pyrolusite (100 to 250 grammes per 100 kg. enamel) is often an advantage for ground enamels, since from experience this addition is known to act favourably upon the adhering properties of the ground enamel. More important, however, is the rôle of pyrolusite for the manufacture of dark violet, black, and metallic-like enamels. For violet enamels an addition of 4 to 7 per cent. of pyrolusite is recommended to one poor in saltpetre. Eventually, 4 to 5 per cent. smalt is added to the raw mixture.

Example of a violet enamel :—

Borax,	140	kg.
Soda,	31	,,
Felspar,	288	,,
Cryolite,	36	,,
Pyrolusite,	20	,,
Smalt,	20	,,
Saltpetre,	0·1	,,
Total,	535·1	,,

By mixing the fused and finely-powdered violet enamel with white enamel a variety ensues which is tinted a delicate rose to lilac.

By addition of cobalt oxide, copper oxide, pyrolusite, and even iron oxide to certain raw mixtures or waste enamels, a beautiful black enamel is prepared.

If the pyrolusite addition be increased in the raw enamel mixture, enamels arise which, after firing, exhibit a peculiarly brilliant metallic lustre. (The pyrolusite content in this case varies between 10 and 12 per cent.)

VIII. CHEMICAL TECHNOLOGY OF TIN OXIDE.

Tin Oxide's Part in the Enamel Industry.—Since tin oxide is of fundamental importance for the white colouring of enamels, and is only inefficiently replaced by some substitutes, or by others which are banned in many countries, a detailed treatment of the subject will now be given. It is absolutely essential that every enameller should not only be acquainted as far as possible with the properties of tin oxide, but also with its manufacture, since enormous quantities are used for enamelling purposes. With this object in view a brief description of the chemistry of metallic tin will now be given.

The word tin is derived from the Latin *Stannum*.* The chief ore for the manufacture of tin is tinstone or cassiterite, which crystallises in the tetragonal system ; the crystals may be short prisms or pyramids, with streaky surfaces. It often occurs in drusy masses, while twin crystals are common. Often, also, it is found massive, granular, or palpable, or in rolled grains, while more seldom it forms delicate fibrous aggregates of concentric structure (wood tin) ; finally, it may occur in angular lumps or in separate loose grains (stream tin).

Beautiful pseudomorphs of tinstone and quartz similar to orthoclase are found at St. Agnes in Cornwall. The crystals are brittle, with a hardness 6 to 7, a specific gravity 6 to 8, and colourless, although generally yellowish-brown to pitch-black. Chemically, cassiterite is represented by the formula SnO_2—*i.e.*, as a peroxide, or also as $SnSnO_4$ (stannic stannate) with 78·62 per cent. tin and 21·38 per cent. oxygen. It generally contains some iron oxide, silica, manganese oxide, or tantalic acid. Before the blowpipe it remains unchanged, but is reduced to tin when heated on charcoal in the reducing flame, especially when a little soda is added. Cassiterite is attacked by alkalies, but not by acids. It occurs in the older granite rocks in reticulated stock works

* See the author's "Beitrag zur Geschichte der Verzinnungs technik," *Archiv. für die Geschichte der Naturwissenschaft und der Technik*, vol. for 1909.

(stock-forming deposits in granite traversed by rich narrow veins), also in zones impregnating the rock and independent of the steep lodes, as at Geier, Zinnwald, Altenberg in Erzgeb, Schlaggenwald in Bohemia, Cornwall in England, or in lodes or thin veins in the country bordering granites and porphyries—*e.g.*, clay slates—in which it is associated with quartz, wolframite, fluorite, apatite, topaz, zinnwaldite, tourmaline, iron pyrites, zinc blende, and molybdenite. The principal localities for it are Altenberg, Geier, Ehrenfriedersdorf in Saxony, Zinnwald, Graupen and Schlaggenwald in Bohemia, Cornwall and Devonshire in England, Penonta, Bretagne, Limoges. It is also found in the younger trachites and andesites (eruptives) of the eastern flank of the Bolivian highlands (Oruro, Potosi), and in the silver, lead, and bismuth sulphide ores, usually without the association of fluorine-containing minerals; also at Campiglia Marittima in a pyrolusite deposit between sedimentary lias, which forms the iron "cap" of the sulphide ore masses. The principal sources of stream tin are in the Malacca Peninsula, the neighbouring islands of Banca, Bilitong, and Karimon, in New South Wales, Tasmania, and the Herbeston district of North Queensland (Australia).* The important localities for tin production are the Straits Settlements, followed by Bolivia, Banca (between Sumatra and Borneo), Bilitong, and Perak, which give very pure tin, known as Straits tin; also in the Isle of Elba, North America, Mexico, Japan, China, and French Cochin China (Tonkin), are found rich tin ore deposits, especially in the region of Cao-Bang, where 1·03 m. of the alluvial deposits yield 5 kg. ore, containing an average of 50 per cent. tin, with some tungsten and gold.

The metallurgical process for converting tinstone to metallic tin is very simple. The ores are first sorted, carefully washed, and the major part of the gangue removed; then they are roasted (to burn off the sulphur and arsenic), and again washed, whereby tin oxide remains behind, since the sulphide impurities are removed as powder. Finally, the oxide is smelted with anthracite to obtain crude tin, which is then refined to pure tin. The alluvial deposits at Banca and Malacca require only a single smelting, on account of the great purity of the ores. The smelting takes place in either a rotatory or shaft furnace (see Fig. 6).

The latter or Saxon method (Altenberg furnace) employs a furnace, which has a single block of gneiss for hearth, with a

* Neumann-Zirkel, *Elemente der Mineralogie*, 1907.

shaft 3 m. high, whose walls are made of granite. In the fore part of the furnace is a crucible where the reduced tin collects, and further away an iron boiler, into which the tin flows from the crucible by means of an opening. The shaft is packed with alternate layers of coal and ore. At the base of the shaft air is

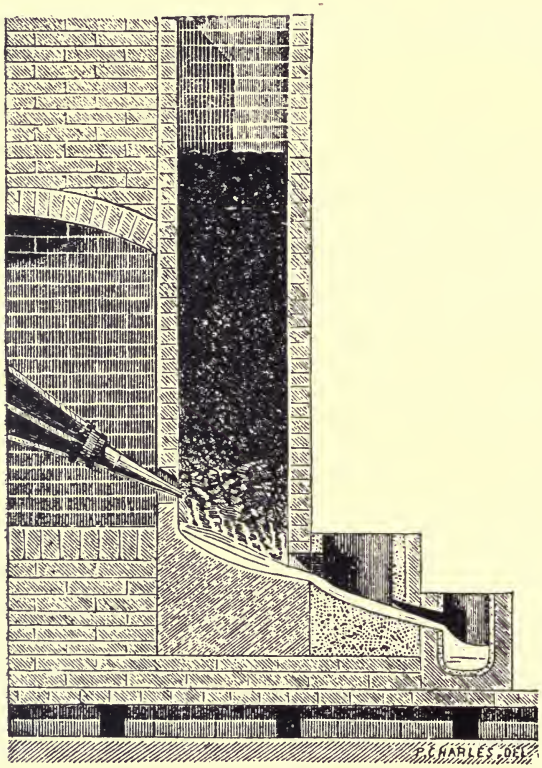


Fig. 6.—Blast Furnace.

blown in through several apertures, and the reduction of the cassiterite occurs by means of the carbon as in the equation :—

$$SnO_2 + C = Sn + CO_2.$$

The fluid metal runs into the iron vessel beneath, while the difficultly fusible alloys of iron and tin remain behind in the shaft. This tin-containing residue is added in the proportion of one-third when freshly charging the furnace. By degrees this

tin slag (tin silicate) will become poorer in tin, and pass into iron silicate and metallic tin.

In England the reduction of the tin ores is carried out in the reverberatory furnace. J J (Fig. 7) are two receivers, into which the fused tin runs. The furnace bed is of pure silica, to avoid formation of tin slag. The furnace is charged simultaneously with ore, small anthracite, and some of the residues from previous reductions (tin slag and scrap tin), while fluorspar is added as

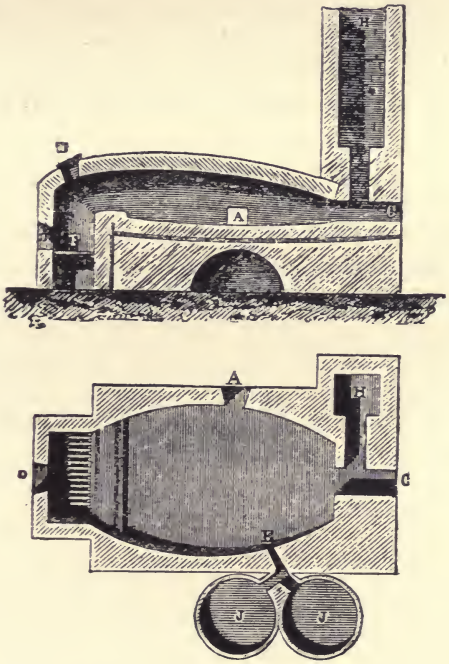


Fig. 7.—Cornwall Furnace.

flux. After closing the doors of the furnace, the contents are heated and raked from time to time, and after five hours the tin slag is withdrawn (and added as one-third of a fresh charge), the reduced tin being allowed to flow into J. After allowing to stand for some minutes, the surface layer is skimmed off and the tin poured into the moulds. In this way the crude tin is obtained, and must be refined for complete purification. Refining is carried out either in the same or a smaller furnace, the tin being heated therein at a lower temperature, when the more readily fusible

tin flows away through an opening. The latter is then closed, the furnace raised to a higher temperature, and a further liquation carried out. The second runnings consist of less pure tin than the first, and are again refined, the final residue being added to the original ore for reduction. Into the pure fused tin contained in the crucible an iron bar is immersed, to which a bundle of green twigs is attached. Arsenic and antimony still present in the tin ore are oxidised, and a "foaming" ensues, due to the escape of steam and gases from the wood (as a result of its destructive distillation). From the agitation occasioned by the foaming the arsenic and antimony are brought to the surface, and thereby oxidised. The pure tin is run off, while the iron alloys remain at the bottom of the crucible, and are submitted to further refining.

According to the following report, which, however, must be received with caution, the cost of producing 100 kg. of pure tin in Saxony amounts to 204 f. 18 c., and in Bohemia 195 f. 73 c., the items being as follows :—

Saxony.

	F.	C.
Cost of raw material,	79	68
Transport, roasting, and mechanical preparation of the ores,	63	0
Smelting and refining,	3	53
General expenses,	7	97
Production cost per 100 kg. tin,	204	18

Bohemia.

	F.	C.
275 kg. washed mineral, delivered dry to the works,	136	39
Fuel for the roasting, smelting and refining, viz. :—		
750 kg. wood,	9	72
425 kg. wood charcoal,	16	85
½ kg. fluorspar,	0	28
Wages and general expenses,	17	80
Tax on tin,	11	63
Production cost per 100 kg. tin,	192	73

A process for preparing absolutely pure tin hails from a French

works,* and consists in starting from crude tin ore or a tin alloy, which is heated in the presence of a gaseous reducing agent (for which hydrogen is the most suitable, since the reduction commences at 500° C.). The oxygen, sulphur, arsenic, and antimony are eliminated by a small excess of hydrogen. After reduction the mass is allowed to cool and the hydrogen stream replaced by one of dry chlorine gas, the heat evolved being advantageously removed by the cooling process. Gaseous tin tetrachloride ($SnCl_4$) is formed, the vapours of which are condensed by passage through cooled worms, and the liquid conveyed to a suitable receiver.

If necessary, the stannic chloride is distilled in presence of a little pure tin (in order to fix the excess of associated chlorine and iron chloride), whereby absolutely pure stannic chloride is obtained.

The stannic chloride is diluted with water in a stone vat, and subjected to electrolysis. Chlorine is evolved at the anode and collected for further use in the process. At the cathode a separation of pure tin in powdery form takes place often accompanied by hydrogen ; this is collected, fused, and poured on to plates, where it solidifies. In cases where hydrogen is formed this is utilised in the process for the reduction of the heated tin ores or tin alloys. The concentration of the electrolyte during electrolysis is always maintained at a definite degree, this being best accomplished by adding gradually a water-free or a strongly concentrated solution of stannic chloride to the bath. The tin then separates in compact masses, and is more suitable for current consumption, since a concentrated solution offers less resistance. It is important that a low temperature be maintained during chlorination (about 100° C.), whereby a redistillation of the stannic chloride is avoided. The hydrogen necessary, or other special reducing agent, may be produced by any convenient process, while the chlorine must be in excess, since the impurities of the tin ore or alloy also consume chlorine.

While the loss in tin by former extraction processes from tin ores usually amounted to from 5 to 15 per cent., almost a theoretical yield should accrue by this method. Tungsten and molybdenum, which frequently accompany tin ores, may be recovered by this process by using a suitable concentration of the electrolyte.

* *Soc. Industr. des Produits Chemiques.*

General Chemical and Physical Properties of Tin.—Tin is an almost silvery-white, strongly-lustrous metal of specific gravity 7·28—*i.e.*, a square metre of tin 1 mm. thick weighs 7,280 grammes. Tin has a crystalline structure, and so crackles on bending (cry of tin), due to friction between the small crystals ; also on pouring hydrochloric acid over a tin surface there is formed a characteristic pattern, due to the same cause. This dimorphism of tin is of far-reaching interest. It had been observed for a long time in Russian shops and museums that massive blocks of tin gradually crumbled to powder. A thorough investigation led to the knowledge of the so-called " tin-pest," which was found to occur gradually on tinned vessels, organ pipes, etc., in the form of pimple-like excrescences, which ultimately became perforations. Cohen, who made a special study of this problem, termed the phenomenon " tin-pest." Tin exists in two modifications—viz., ordinary tin of specific gravity 7·3, and a grey powder of specific gravity 5·8—therefore, during transition into grey tin (pest-infected tin) a swelling takes place, as if it were covered with small abscesses.

The formation of grey tin takes place below 20° C. Below this temperature, therefore, the tin is really in unstable (labile) equilibrium, so that tin-pest is of constant occurrence in cold countries. Above this temperature metallic tin is stable, and, if the grey infected tin be remelted, metallic tin is once more obtained.

At 20° C. tin is said to possess a transition point, and the formation of grey tin may be artificially developed by contact with tin already infected (inoculation of the tin), especially when moistened with pink salt (tin-ammonium chloride). This was established by the dilatometer test with Cohen's transition element.

R. v. Hasslinger has observed a new tin pest, which he describes in the *Wiener Monatsheften der Chemie*, the case being noted of a tinned iron vessel, which for two years had been exposed to warm, though never boiling, water, being completely full of cracks after this period. This phenomenon would occasion no surprise to the majority of people, who would merely throw the useless vessel on the rubbish heap. The chemist, however, must find the reason for such an occurrence, and a similar state of affairs is assumed, as in the case of bronze disease or bronze pest. With pure tin, also, such alterations had already been noticed. The special point in this case is that the cause of the disease was

inoculation. When tin objects are brought into intimate contact with tin already diseased, they are infected, and themselves begin to disintegrate. Hasslinger observed that this particularly infectious tin disease attacks a space of half a centimetre radius during a day. It can also be communicated to tin foil, which, owing to its very small thickness, is very speedily perforated. Warming the vessel does not arrest the progress of the disease.

The sole means of saving the metal is by remelting it. The comparison of tin pest with human illness is not unnatural after this description, since the symptoms throughout are similar to the case of a bacteria-propagated epidemic.

Metallic tin is soft and very malleable (stanniol). At 200° C. it becomes brittle and may be powdered. It melts at 231° C., and distils at a white heat (about 1,700° C.). When heated in air tin burns to form white tin oxide.

The purity of tin is judged in the trade by the following tests :—

(1) The purer the tin, the louder the crackling noise on bending.

(2) By comparison of the weights of two masses of tin having the same shape, but one of which is pure.

(3) By fusing the metal at a very low temperature and running it into a semi-spherical mould 1 to 2 cm. in diameter. Pure tin cast into sheets or ingots exhibits on cooling a perfectly smooth surface, which exhibits no signs of crystallisation. Traces of impurities (lead, etc.) cause needle or star-like patterns to occur on the solidified surface, and the greater the content in foreign metals the more pronounced the patterns. Moreover, impure tin is duller and less lustrous on the surface. With the exception of Banca, Bilitong, and Malacca tin, most varieties enclose small impurities of copper, lead, iron, or arsenic.

If we assume the thermal conductivity of silver to be 1,000, that of tin is 145, while its electrical conductivity is 11·3 if silver is 100.

The thermal capacity of tin is 0·0562, and its malleability is between copper and platinum.

After fusion tin suffers a diminution of—

$$\text{Length } \frac{1}{a} = \frac{1}{128} = 0{\cdot}0078,$$

$$\text{Surface } \frac{2}{a} = \frac{1}{64} = 0{\cdot}0156,$$

$$\text{Volume } \frac{3}{a} = \frac{1}{43} = 0{\cdot}0234.$$

If the volume of the mould be unity, that of a tin cast will be $1 - \frac{3}{a} = \frac{42}{43} = 0{\cdot}9766$.

The weight of a piece of cast tin is obtained by multiplying the mould weight by 0·9766.

Statistics.—Import and export of tin ores, tin, and tin oxide in kg. for 1910.

Tin Oxide.

	Import.	Export.
Germany, . .	43,000 kg.	118,400 kg.
Austria-Hungary, .	6,000 ,,	70,000 ,,
Italy, . . .	48,200 ,,	600 ,,
France, . .	41,600 ,, (1908)	48,300 ,,

Tin Ores.

Germany.—Import (1910), 17,343,000 (about 9,970,800 kg. in the year 1907), of which there came from

England, ...	523,200 kg.
Spain, ...	598,400 ,,
Bolivia, ...	9,135,600 ,,
Chili, ...	881,900 ,,
Mexico, ...	87,100 ,,

Export (1910), 72,000 kg., of which the amount to England was 2,600 kg., and to Austria-Hungary 2,200 kg.

France, ... { Import, 1,109,800 kg.
Export, 357,900 ,,

Metallic Tin.

Germany, . . { Import, 14,297,000 kg.
Export, 7,530,000 ,,

Austria-Hungary, . { Import, 4,569,000 ,,
Export, 547,000 ,,

Netherlands, . . { Import, —
Export, 15,429,000 ,,
(from Colonies).

As an important tin-producing country Bolivia now merits attention, and it has partly to thank its richness in tin ores for its prosperity.

In the year 1907 Bolivia exported 27,677,780 kg. raw tin (termed " Barillas "), although this only possessed an average content of 60 per cent. tin, corresponding to 16,606,668 kg. of pure tin. Seven departments participated in this production, viz. :—

Potosi, Uyani, Tupeza, Colquechana, with	16,314,664 kg.
Oruro, with	9,476,287 ,,
De la Paz, with	1,810,736 ,,
De Cochabamba, with . . .	76,093 ,,
Total, . . .	27,677,780 ,,

This export is correspondingly taxed, and secures to the State of Bolivia a revenue of 2,807,142 francs.

Oxygen Compounds of Tin.—Tin is very resistant towards atmospheric agents, weak acids, and alkalies. It gives rise to two series of chemical compounds, which are derived from tin monoxide or stannous oxide, SnO, and tin dioxide or stannic oxide, SnO_2. The latter are more stable than the former. For enamelling purposes only stannic oxide, SnO_2, is important.

Stannic oxide consists, when theoretically pure, of 78·67 per cent. tin and 21·33 per cent. oxygen.

From this oxide two hydroxides are derived—viz., the stannic acids H_2SnO_3 and H_4SnO_4. Each of these two acids exists in two forms, which are distinguished from one another in behaviour (Berzelius, 1811, and Gay-Lussac, 1817).

One distinguishes ordinary or α-stannic acid (H_2SnO_3 or H_4SnO_4) from meta- or β-stannic acid (H_2SnO_3 or H_4SnO_4).

The metastannic acid is obtained by dissolving metallic tin in nitric acid of specific gravity 1·35 = 37·4° Bé (1 litre of this acid contains 772 grammes of concentrated nitric acid = 48½° Bé.).

This was the former, but now seldom used, method for the production of stannic oxide in the wet way. By heating this metastannic acid, water is expelled and tin oxide remains behind. For many purposes where only small quantities of stannic oxide are required (for decorative enamels), this is prepared in the wet

way by the slow action of dilute nitric acid on small pieces of tin in a glass or porcelain vessel. Obnoxious brown fumes of oxide of nitrogen are evolved, and the tin is converted into white metastannic acid. This is filtered off, washed with hot water on the filter to remove excess of nitric acid, and then levigated with much water so that the finest milky-white particles are removed, while a part of the still undecomposed metallic tin remains behind in the form of fine specifically heavier nodules enclosed by stannic acid. The fine powder obtained by levigation is allowed to stand and settle, the water is decanted, and the metastannic acid dried and heated to redness in order to obtain pure white anhydrous stannic oxide.

$$H_2SnO_3 - H_2O = SnO_2.$$

The stannic oxide so prepared is specifically heavier than the oxide obtained by the oxidation fusion in the reverberatory furnace, and, therefore, does not mix as intimately with the enamel, while the consumption is greater, corresponding to the smaller volume, than if ordinary stannic oxide were used.

As already mentioned, stannic oxide prepared by the wet method now plays an entirely subordinate part.

The ordinary or *a*-stannic acid is obtained by addition of alkali to freshly prepared solutions of stannic chloride ($SnCl_4$), as a white voluminous powder which is readily soluble in mineral acids and in caustic-soda solution. In hydrochloric acid solution the *a*-stannic acid changes by degrees into the more stable meta-stannic acid.

The metallic salts of stannic acid (the so-called stannates) are stable. Stannic oxide is fusible in the electric furnace, insoluble in acids and alkalies, and non-poisonous.

The Manufacture of Stannic Oxide.—The industrial production of stannic oxide is carried out at the present time by many processes, which in principle are based upon the surface oxidation of metallic tin by atmospheric oxygen. Another method in principle is that tin is heated in finely divided condition (*e.g.*, dust) to the oxidation temperature, and then brought into contact with a current of air.

Three modes of preparing stannic oxide must be distinguished ; first, the production by dry oxidation in the reverberatory furnace ; second, the oxidation of molten tin sprayed into the open flame ; and third, the preparation from scrap tin derived from tin waste.

While oxidation in the furnace is the most certain method of preparation, since the process may be regulated and thereby a marketable product for all purposes obtained, the repeatedly patented spraying process is beset with numerous vicissitudes, while the tin oxide so obtained is unsuitable for cast-iron enamels. The production of tin oxide from sheet tin waste has not up to the present attained economic standing, although the stripping of tin waste has been an important branch of industry for about twenty years, especially for the production of tin chloride. In addition, there are chemical difficulties of such a technical character in the preparation of pure tin oxide for enamelling purposes as to prevent a serviceable tin oxide being placed on the market. These difficulties originate from the numerous impurities introduced during the electro-chemical treatment of tin waste, which are both difficult and expensive to remove completely. The hope for improvement and progress is not, however, excluded.

Some of the best known and most interesting of the numerous patents of recent years will now be briefly described.

A process by Hermann Mühlinghaus * (D. R. P., 214,735, Kl. 40*a*, Gr. 44) consists in the combined action of carbon and air upon tin-containing material, so that the volatilised tin oxide is withdrawn before layers are formed which prevent penetration. The raw material after fusion is conducted to a furnace in which the volatilisation is brought about by the action of coal and air, an outlet being provided for the immediate exit of the volatile stannic oxide (see Fig. 8). Proposals have been made earlier for heating ores or tin slags in finely-divided condition with coke, then blowing in a current of air to convert the reduced tin to stannic oxide; also to treat molten or melting slag with excess of reducing agent in presence of air.

It appears advantageous to shorten the path of the oxidation products from the liquid tin ores or slags, and this is carried out as follows :—Fig. 8 is a section of the furnace. The tin-containing materials are fused with or without reducing agents as desired, and the process of the invention first begins with the use of molten tin-containing materials. The latter are taken from the furnace *a* into a lower one *b*, which is permanently charged with coal, coke, anthracite, etc., and at *h* air is introduced (under pressure if possible). The stannic oxide thereby formed is driven by the air current through *g*, or so that the molten tin is oxidised

* This process could scarcely be adopted.

to tin oxide, since the tin oxide compounds contained in the mass experience a double decomposition ; first, a reduction to tin and simultaneously (*in statu nascendi*) an oxidation and volatilisation to tin oxide.

This process has the advantage that the volatile tin oxide need not penetrate into the molten mass during preparation.

In Fig. 9 an example is shown where the process can be carried out to the fusion of the tin materials without reducing agents. An electric furnace *o* is here provided for carrying out the fusion (additions may be made to render the fusion easier). The reduction-oxidation process takes place between 1,300° and

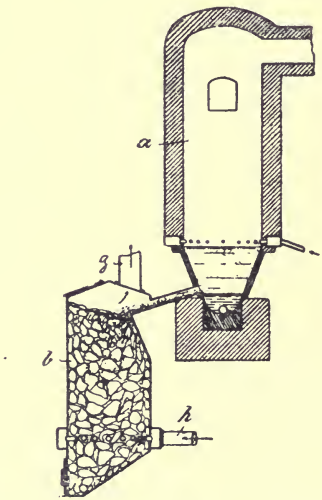


Fig. 8.—Furnace for Manufacture of Stannic Oxide.

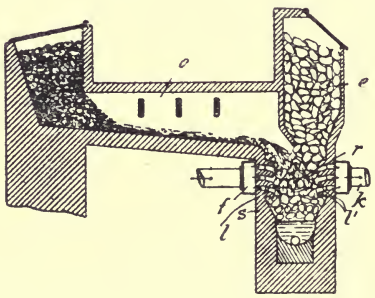


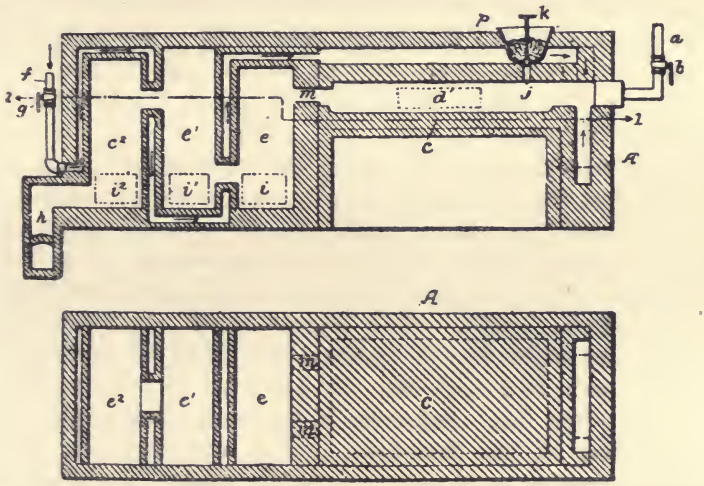
Fig. 9 —Electric Furnace for Reduction-Oxidation of Tin Materials.

1,500° C. After melting, the tin is conveyed into the narrow receiver, to which an air holder *f* is attached at *s*, whereby, through the grate *l*, air may be forced or withdrawn through the receiver.

The stannic oxide passes by the rear grate *l'* into the channel *k*. Through the top *e* coke enters continuously into the receiver beneath, and over it is discharged the liquid slag from the electric furnace. The process may also be carried out in a Bessemer converter, in which air mixture with coal dust is forced through the apertures of the converter into the tin-containing melt. According to this process up to 0·18 per cent. of the total tin present in the raw material is converted into stannic oxide.

A process protected by the Elektrizitats-gesellschaft of Gelnhausen (D. R. P., 116,758, Kl. 12*n*) for the preparation of stannic oxide introduces the tin in powdered form into a current of heated air, whereby the oxide layer arising on every tin particle extends throughout to its centre, and the tin is accordingly transformed at a single operation entirely into the oxide. At the most the diameter of a tin particle should be only 0·1 mm.

A similar process is that of L. Fink-Huguento (Belg. Pat., 179,151, of Aug. 25th, 1904), in which an apparatus serves for the direct combustion of dust-fine tin, which is continuously sprayed in.



Figs. 10 and 11.—Vertical and Horizontal Sections of Combustion Furnace; Foersterling's Process.

Another method proposed by H. Foersterling, of Perth-Amboy (D. R. P., 173,774, Kl. 12*e*, Gr. 9), heats metallic tin in a combustion furnace in presence of air which has been previously heated by a flame spreading over the hearth. The temperature attained is sufficiently high to prevent the formation of discoloured stannous oxide, the stannic oxide produced being continuously removed from the furnace.

Fig. 10 shows the vertical section, and Fig. 11 the horizontal section along the line 1—1 of Fig. 10. A pipe *a* leads to the furnace A, through which gaseous fuel (generator gas, etc.) is conveyed, regulated by means of the valve *b*. The tin is melted in *e* and the oxide withdrawn at *d*.

m (Fig. 11) connects the metal furnace with the chambers *e*, *e'*, e^2, in which the stannic oxide is collected. Between the double walls of the chambers the air is previously heated to a high temperature before entrance into the melting section. Air enters at *f*, and mixes with the gases evolved from *a*. The ventilator *g* regulates the air entrance. The furnace containing the tin is heated from 700° to 1,100° C., the oxide removed through *d*, and fresh tin added at short intervals. The oxide driven into the chambers *e*, *e'*, e^2 is removed through *i*, *i'*, i^2. The previously heated air contributes to the temperature elevation and to the formation of the white stannic oxide.

A similar process was patented by Wassermann and Jaeger (D. R. P., 34,653, Kl. 12), in the year 1885, whereby the tin was melted in a closed muffle, having an air pipe in the rear and chambers connected in front, which lying in the furnace is surrounded by flame.

The replacement of the oxidised tin ensues through a fireclay pipe dipping into the metal bath. A current of heated air is forced through the metal bath, and the stannic oxide thereby formed is blown direct into the front chambers, thus avoiding a chimney loss. By this continuous blast the metal bath will always remain bright, while formation of stannous oxide is rendered impossible by the excess of air. The tin particles mixed with the oxide flow back into the bath, as the pipe leading from the muffle into the chambers is inclined. Only pure stannic oxide arrives in the chambers, and a supplementary grinding, sieving, levigation, and reduction of the residue is unnecessary.

Drs. Rickmann and Rappe (D. R. P., 99,165) propose an addition of silicofluoride of tin or cerium (5 to 25 per cent.) for rendering enamels opaque.

A process by Lomax * employs a furnace based on the Gérard principle, whose floor consists of a horizontal canal provided with two hollows, in which the almost cold metal stands in contact with five or six electrodes. A very high temperature is maintained in those parts of the canal lying between, and here a current of cold or hot air is expelled from three or four pipes, which forms the oxide and drives it into a special receiver. Lomax claims to obtain pure stannic oxide, SnO_2, if air at 400° is blown into tin at 1,200° C.

Charles Paul Bary, of Paris, has patented a process for the

* *L'Ind. électro-chim.*, 1903, vol. vii., p. 69.

production of stannic oxide (Austrian Pat., No. 4,370, Kl. 12, June 10th, 1901), which consists in heating metallic tin in absence of air to about 1,700°, and conveying the tin vapour into a neighbouring chamber, where it meets a heated air or oxygen current, ignites, and burns to stannic oxide. The temperature of 1,700° C. can be produced in ordinary furnaces (?), or regenerative furnaces, or best in the electric furnace. The tin oxide so received should be very uniform and extremely fine. The finer the granules of oxide the more efficiently can a smaller amount produce opacity in the enamel upon large surfaces. According to this process pure tin oxide ready for use may be produced in one operation.

Tin oxide plays a dominating rôle as an opacity agent for enamels, glazes, and glass ware. The numerous substitutes to be discussed later have not altered the situation in the slightest degree, since either their turbidity strength stands in no correct relationship to the price, or in consequence of strict hygienic regulations in many countries respecting compounds of lead and antimony for the preparation of enamels for kitchen utensils, their employment is limited. We shall see, however, that frequently technical difficulties attend the use of such substitutes.

The circumstance that enamel in contrast to earthenware and Fayence industries has been made absolutely independent of lead compounds, has contributed materially to its development. It has been noted earlier that tin compounds are absolutely uninjurious and non-poisonous, and in the Middle Ages men went even so far as to ascribe medicinal properties to tin.

After the abandonment of the primitive method for preparing stannic oxide, and the manufacture of this important article by chemical firms on the large scale, the management of one of the latter, supplying enamel works with tin oxide, undertook the erection of works near Cologne specially constructed for this purpose. This venture was soon joined by other undertakings of like nature, and with the extension of the enamelled ware industry the number grew to such an extent that overproduction was a natural consequence, leading to an extraordinarily ruinous competition in prices. Being hard-pressed, a number of these firms in 1898 united to form a syndicate, which, however, did not long enjoy the fruits of a general policy of price regulation, for soon afterwards new international candidates appeared in

the shape of undertakings in Germany, England, France, and America for working patented processes, so that to-day more than twenty different firms are seeking to capture the tin oxide market.

This unusually large number of firms producing stannic oxide is due partly to the fact that there are always people who either themselves calculate on extraordinary profits or are persuaded that such will accrue by business speculators. Yields much too high are continually expected, misled by the simple chemical formula of stannic oxide, and much too small equipment charges estimated, no attention being paid to the uncertainty of the price of raw tin, which, through sudden market fluctuations, may render illusory the best firm's arrangements. At this stage the question must also be discussed as to whether it would not be more suitable to produce stannic oxide in the works itself. The author, on the ground of many years' experience in the most important of European works, can only answer the question in the negative. In earlier years most of the large enamel firms were accustomed to prepare their own tin oxide, and to-day this is still the case in some works either where independence from some special firm is desired, or to utilise the furnace equipment more ; it may be, however, that no account is taken of the cost of producing the tin oxide, and that the operation is conducted by out-of-date methods in some obsolete apparatus situated in an odd corner of the works, whereby a not inappreciable amount of stannic oxide escapes up the chimney either through too high a temperature or too vigorous a draught. Briefly, in such a works the cost of production is often fluctuating and quite beyond control, while between theory and practice there exists an almost unbridgeable chasm. There must also be taken into account the amount of tin lost through dishonest employees, and also by unskilful treatment of the slag and scrap tin.

In many enamel works a part of the tin is recovered from the residues of the oxide manufacture by reduction, and this frequently by extraordinarily primitive methods, the slag being rejected as worthless or sold dirt cheap. It is an obvious conclusion, therefore, that a modern enamel works should not engage in stannic oxide manufacture, since this is not only a branch industry, but requires special attention to achieve technical perfection. On the other hand, a chemical firm which is exclusively engaged in the production of tin oxide can concern itself with the

technical and commercial superintendence, the control of the import and export, the study of the tin market, the testing of new processes, and with laboratory research for the utilisation of residues in the best possible way. No self-producer could compete in price with such a specialised firm.

Moreover, in consequence of his greater output and exclusive occupation with a single product, the maker of tin oxide on the large scale is in a position to judge the tin market correctly, and to meet his tin requirements on favourable terms. At the present time the large makers deliver tin oxide, not only at prices which afford only an exceedingly small profit, but with such perfection as would be sought for in vain in those enamel works producing their own tin oxide. As a rule, the tin oxide is of such an enhanced value that many a large enamel works, which earlier produced its own tin oxide, has frequently been compelled to purchase the same from specialists when enamelled wares of special beauty had to be produced. Again, from the standpoint of the enamel technologist, there is nothing more acceptable than a good tin oxide ready on demand, rather than to be compelled as formerly to store large consignments of expensive tin. Should a sample be unsatisfactory, a case of rare occurrence, it is merely returned to the vendor, while in the case where the enamel firm produces its own tin oxide the situation must be faced that some time or other the quality of the oxide will leave much to be desired. After this necessary deviation, the rôle of tin oxide in the enamel will again receive consideration.

In earlier days, and sometimes even now, the tin oxide was not employed alone, but mixed with lead oxide in the so-called "Calzine," which was made by oxidation and fusion of a tin-lead alloy. Calzine, however, does not concern a modern enamel firm.

A large portion of the total amount of tin oxide was formerly added to the crude enamel mixture, and the whole fused together in the furnace. Experience, however, has now shown that it is more rational to add the tin oxide only at the wet grinding of the enamel, since on melting the mixture a part of the tin oxide at the high temperature prevailing in the furnace is transformed into the non-opacity producing tin silicate, while a smaller amount of the tin oxide may also be volatilised. It is known that the covering power—*i.e.*, the opacity of a white enamel—is rendered smaller by the practice of pouring the fiery molten

glaze into cold water (splintering) after the fusion than when the fused white enamel is allowed to run from the furnace without such water treatment. This fact probably depends, so far as tin oxide comes into the question, upon a physical change, such as occurs in the formation of gold-ruby glass or yellow enamels by means of cadmium sulphide. The author found, for example, that an addition of cadmium sulphide to the raw mixture after melting only colours the enamel yellow, if the latter is cooled slowly and has not been splintered in water. It is a fact, however, that the yellow colour develops after covering and firing the ware enamelled with it, since the finished article cools relatively slowly. The cause may perhaps be in the uneven distribution of tin oxide by rapid cooling of the fused enamel, whereby large quantities remain in solution. In general the assumption must be made that the tin oxide is not dissolved in the enamel, but finely distributed in suspension, and that it is this property which gives the extraordinary opaque effect produced by tin oxide in glazes and enamels.

Only at the high-melting and firing temperatures in the melting and muffle furnaces respectively is a part lost by formation, as previously mentioned, of a fused transparent tin silicate. A white enamelled ware, which has been too strongly fired, diminishes, therefore, in opacity, and appears less white; the ware is then said to have been "burnt."

A further inexplicable fact, well known to the practical enameller, is that a white enamel mixed with tin oxide ground moist in the ball mill appears less white than the same enamel ground in small wet stone mills. Ball mills are, therefore, less fitted for grinding white enamels in spite of their undoubted superiority as regards output. The tin oxide addition at the mill varies in general from 6 to 14 per cent. of the weight of the fused enamel.

Enamel recipes with under 6 per cent. of tin-oxide addition are to be regarded sceptically for better-class purposes. When the addition at the mill exceeds 16 to 20 per cent., an appreciably higher covering power does not take place, and any addition above the 20 per cent. limit is, therefore, regarded as waste, the more so as the enamel thereby deteriorates in beauty and lustre. Tin oxide undoubtedly causes the enamel to be more viscous.

White enamels serving for the first coat should, as a rule, be whiter than the so-called second white, which should only

confer lustre to the ware. Nevertheless, diverging opinions are held on this point among experts.

As a rule, only first-class tin oxide prepared from the purest tin should find employment, and every consignment should be tested, since there are two modifications of stannic oxide which can appreciably vary in behaviour according to the mode of preparation of the tin used (whether pure, refined, or electrolytically produced).

Small black specks * may often be detected in the enamel after covering and baking, which spoil the general appearance of the wares. These may be traced to dust, magnesia, etc., but, as a rule, they consist of particles of unoxidised metallic tin, which may easily be present in imperfectly prepared stannic oxide. As soon as these defects are noticed, the following test should be made :—One kilo. of the stannic oxide should be washed with water, or, better, should be made into a paste and water added to it with vigorous stirring, allowing periodic settling intervals of about 10 seconds each. The stannic oxide is removed by the water, and the washing continued with greater and greater caution until the decanted water appears clear, and at the bottom of the vessel a grey granular residue of metallic tin remains behind, since this, being specifically heavier than the oxide, settles more quickly during the washing. This residue is collected, dried, and weighed, and the vendor who supplied it made answerable for the discrepancy. In many samples of stannic oxide the presence of up to 20 grammes of metallic tin per kilo. may be proved—*i.e.*, 2 per cent. During the manufacture of stannic oxide it may happen that particles of tin are only oxidised superficially, and the interior may still be a nucleus of tin. In consequence of this tendency the stannic oxide is repeatedly sieved and heated to redness in a special furnace during manufacture.

The finer the grains of stannic oxide are, the more and the better will their distribution be in the enamel, since the opacity action of tin oxide is a function of its available volume. The coefficient of expansion of an enamel does not appear to be essentially altered by the addition of stannic oxide, although the fusibility is rendered easier.

The maximum addition can be taken at 20 per cent., above which no increase in covering power takes place, while, on the

* J. Grünwald, *Theory and Practice of Enamelling on Iron and Steel.* C. Griffin & Co., London, 1909.

contrary, the lustre and physical properties of the enamel are so prejudiced that it is almost unserviceable.

In general, it is more advantageous to work with a single thin coating of white enamel of good covering power (*e.g.*, with 10 to 20 per cent. SnO_2), instead of two coats each with 6 per cent. stannic-oxide content. Unfortunately, practical difficulties are encountered when this is adopted. The thinner the enamel layer with equal covering power, the more durable is the enamelling.

IX. OTHER WHITE COLOURING AGENTS.

Antimony Oxide and Sodium Meta-antimonate.—The starting point for the preparation of antimony oxide is metallic antimony (Stibium = Sb). The metal itself is obtained from the mineral stibnite (antimony sulphide, Sb_2S_3) by roasting this in the furnace in presence of air.

$$2Sb_2S_3 + 9O_2 = 2Sb_2O_3 + 6SO_2.$$

The oxide is then heated to redness with coal and thereby reduced to metal. The latter is also obtained by heating the sulphide with iron, when the antimony settles down as a regulus beneath the sulphur (precipitation process).

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS.$$

The antimony so obtained is purified by melting it repeatedly with saltpetre, whereby arsenic, sulphur, and lead are removed.

Antimony forms a series of oxygen compounds—*e.g.*, the trioxide Sb_2O_3, antimonic anhydride Sb_2O_5, and the tetroxide or antimono-antimonic oxide, Sb_2O_4 or $Sb_2O_3 . SbO$.

The trioxide (usually termed antimony oxide) or antimonious anhydride, is formed similarly to stannic oxide by burning antimony in air, or by oxidation with dilute nitric acid. The oxide and hydrate dissolve in potassium or sodium-hydroxide solution, forming salts which decompose when the solutions are evaporated. By more vigorous oxidation the pentoxide results, and this is also formed when meta-antimonic acid is heated at 275° C. The trioxide, as also the pentoxide, passes into the tetroxide at a red heat. Antimony trioxide is yellowish in colour, and imparts this to enamels, whilst the tetroxide, which is the most stable of the antimony oxides, is pure white.

Sodium meta-antimonate comes on the market from its makers, Drs. Rickmann and Rappe, under the name "Leukonin," and possesses the formula Na_2SbO_3. Leukonin contains, in addi-

tion to sodium meta-antimonate, small quantities of antimono-antimonate (Sb_2O_4). In order to test whether leukonin contains antimony oxide the method of Bunsen and Rose is recommended. The sample to be examined is treated by this method with caustic potash solution, and silver nitrate added to the solution obtained in presence of excess ammonia. If antimony oxide be present a separation of silver oxide ensues.

Leukonin is insoluble in water, alkalies, and acids, but somewhat soluble in boiling concentrated sulphuric acid, *aqua regia*, and tartaric acid solution. 100 parts of dried leukonin contain 69·16 parts of metallic antimony. The patent of Drs. Rickmann and Rappe (D. R. P., 134,774, Kl. 12*i*, Aug. 14th, 1901) reads as follows :—

"In the preparation of alkaline antimonates on the large scale the inconvenience arises that the antimonate formed by known methods from antimony, antimony oxide, or antimony sulphide by means of saltpetre and alkaline hydroxides, occurs as a discoloured, sintered-together mass. Such a preparation is unserviceable for many objects, such as the white colouring of glass, enamels, and glazes. For this purpose the alkaline antimonate must be a white amorphous powder, and such may be obtained on an industrial scale by adding to the melt a large quantity of a substance, such as common salt, soda, etc., which itself takes no part in the reaction. By this device the alkaline antimonate remains behind after lixiviation as a white, amorphous mass. This presence of compounds, inert as regards the reaction, causes this to be more prolonged, and prevents the sintering together of the alkaline antimonate, while it is also protected against the reducing action of the fuel gases.

"*Patent Claim.*—The process for the preparation of alkaline antimonates in the form of a light, white, amorphous mass is characterised by the addition of compounds not taking part in the reaction, such as alkaline chlorides, carbonates, sulphates, or similar bodies, to the reaction mixture consisting of antimony, antimony oxide or sulphide, and alkaline hydrates *plus* saltpetre."

Contradictory opinions prevail as to the use of antimony oxide and antimony preparations for producing white opaque enamels, the discussion of which, however, is beyond our scope.

The German regulations of June 25th, 1887, and July 5th, 1887, were very strict concerning the hygienic conditions for

vessels used for eating, drinking, and cooking purposes, and at the same time very indefinite, since almost the whole of the metals are forbidden, owing to the impression that their coloured compounds have an injurious character, these including, not only antimony, but tin, which is certainly harmless. Fortunately, § 2 of the regulations cited relaxed this foolish limitation, since in § 2, paragraph 1, it states that for the preservation or packing of foodstuffs intended for sale, vessels, wrappers, or protecting covers, for whose preparation pigments are employed, the following are forbidden—viz., antimony, arsenic, uranium, lead, cadmium, chromium, copper, mercury, zinc, tin, etc., with the exception of chromium oxide and stannic oxide.

In the same § 2 it further states in conclusion that "for all colours burnt into glass, glazes, or enamels, and for the exterior painting of vessels by waterproofing materials, the regulation does not hold." (§ 2, paragraph 1, Prohibition of certain colours.)

The property possessed by the oxides of the group, tin, antimony, and arsenic, of rendering enamels opaque, reaches its maximum effect in stannic oxide.

While the reasons are easily understood why arsenic is excluded for enamelling purposes (only a few English sign-painters and cast-iron enamellers still work with enamels containing arsenic), yet, on the other hand, the use of antimony oxide is also technically limited, for, according to the author's experience, an addition of antimony oxide exceeding 3 to 4 per cent. makes the enamel of less covering power, while it becomes soapy, defective, and easily liable to chip.

The rational use, however, of antimony oxide for making white enamels and for producing a really good effect requires particular chemical conditions during enamel mixing, and these are naturally the secret of a few experts only.

The soluble antimony salts are undoubtedly poisonous, but the particular circumstances under which antimony oxide may be dissolved out of enamels cannot be dealt with here.

The Austro-Hungarian, German, and Russian enamelling firms are absolutely opposed to the use of antimony oxide.

Titanic Acid and Rutile (TiO_2).—Rutile is found in tetragonal crystals, frequently also in compact, splintered, or granular aggregates, but more often in sands as a secondary deposit with quartz, crystalline schists, granites, and chalk. It occurs at Krummhennersdorf near Freiberg, Bärnau in Bavaria, Sanalpe in

Carinthia, Modriach in Steiermark, Arendal in Norway, Buitrago in Spain, Takowaya and Tjoplyie Kljuci in the Urals, and Minas Geraës in Brazil. Its colour is reddish-brown, or hyacinth-red to dark blood-red, or often yellowish-brown to black (Nigrin). Rutile possesses a metallic, adamantine lustre, and is non-transparent. Its chemical formula is $Ti_2O_4 = 2TiO_2$, with 61·15 per cent. titanium, 38·85 per cent. oxygen, and usually 1·5 per cent. iron oxide. It is infusible before the blowpipe, unattacked by acids, and renders glass or enamels opaque.

For a long time it was difficult to obtain large quantities of pure white titanic acid, TiO_2, from rutile.

A patent by Carl Dreher (D. R. P., 13,192, Kl. 12*i*, of Sept. 2nd, 1903), contains the following recipe :—

100 grammes rutile are treated with a warm solution of

a { 100 parts concentrated sulphuric acid,
300 ,, sodium bisulphate,
1,000 ,, water.

After filtration from the insoluble residue, the solution is electrolysed in a cell having a porous pot as diaphragm, the above solution *a* as cathode liquid, and acidulated water for anode liquid. Both electrodes are of lead. The solution, which is at first weak grey in colour, gradually becomes blue, whereupon soda solution (90 per cent. of the necessary amount for neutralisation) is added. All the titanium is thereby precipitated free from iron, and the bluish precipitate is filtered and washed repeatedly with water and a little bisulphate. The washed precipitate when dried in air is white.

A further stage in the preparation of pure titanic acid and its use for enamel manufacture is attained by the patent of Drs. Hillringhaus and Heilmann, of Güstrow (D. R. P., 207,011).

Use of Titanic Acid for producing Opaque Enamels.—Titanic acid, when added in certain proportions, develops opacity in enamels, and the shade produced is mostly greyish to yellowish-white. Laboratory experiments with the product are not yet concluded. Vondracek recommends the following mixture for transparent glazes :—

15 to 30 parts sodium nitrate, 116 soda, 33 to 50 limestone, 60 to 360 quartz, 62 to 83 boric acid, and 20 to 80 titanic acid, or 15 to 30 parts saltpetre, 116 soda, 100 limestone, 240 to 360 quartz, and 20 to 80 titanic acid.

For enamels:—15 to 30 parts saltpetre, 116 soda, 100 chalk, 60 to 180 quartz, and 80 titanic acid.

This enamelling, however, did not attain the desirable efficiency.

Wuppermann (Austrian Pat., 5,560) has patented the use of artificially-prepared white titanic acid for making white enamels. According to the above, an addition of 10 per cent. suffices, but practice has not confirmed this idea, especially on account of the yellow to greyish colour imparted to the enamel.

According to Drs. Hillringhaus and Heilmann, this colour defect may be removed by the addition of small quantities of cobalt oxide, or by using the titanic acid in the form of barium titanate, which has been heated to redness before use (900° C. and over).

The covering power of such an enamel should be sufficient, although blistering occurs in places.

The product is supplied as a mixture of barium nitrate and titanic acid, and must be heated to redness before use in order to obtain barium titanate. The amount of this addition is given as 7 per cent. The titanium-containing enamels should be more resistant to moisture and acids, although, according to Eyer, they are brittle.

Salts of titanic acid have also been recommended for opaqueing purposes—*e.g.*, in Eng. Pat. 12,583, 1907, H. W. Loke advises calcium and barium titanates mixed at the mill with tin oxide and phosphates (5 to 10 per cent.).

Other Substitutes for Tin Oxide.—The series of products proposed is considerable. As such come under consideration:—

Calcium Phosphate (Bone Ash).—The opaqueing action of bone ash, and still more pronounced of the chemically-prepared substance, has long been known. Should this compound be used instead of stannic oxide, the amounts to be added, owing to the relatively small opacity produced by the phosphate, render the enamel almost unserviceable. Moreover, the lime content is injurious, and a limited addition of bone ash easily brings about blister formation on the enamel. R. F. Wagner (D. R. P., 196,897) recommends aluminium-fluoride, while H. Schwarz * advises zinc fluoride. Even lime and asbestos have been proposed by Reimann (Amer. Pat., 851,317). (100 parts sand, 42 soda, 20 asbestos, 1 arsenic, 4 saltpetre, 20 lime.)

* *Verhandlungen zur Beförderung des Gewerbefleisses*, 1877, p. 117.

According to Hermsdorf and Wagner's patent (D. R. P., 166,672), white, opaque, easily fusible glazes are obtained with calcium phosphate, if the addition of the latter be delayed until the last moment—namely, until firing the enamel. For this purpose two separate glazes are fused, one containing phosphoric acid and the other the calcium compound. The two glazes are then mixed in corresponding proportions and finely-ground at the wet mill. The inventors give the following data :—

Glaze I.—K_2O 9·2 per cent., Na_2O 14·3 per cent., alumina 10 per cent., phosphoric acid 14 per cent., boric acid 13·8 per cent., silica 40·4 per cent., nickel oxide (for ground) 0·4 per cent.

Glaze II.—K_2O 5·3 per cent., Na_2O 14·3 per cent., sodium fluoride 5·2 per cent., aluminium fluoride 3·5 per cent., alumina 5·9 per cent., calcium fluoride 16·9 per cent., boric acid 14·9 per cent., silica 33·6 per cent., nickel oxide 0·4 per cent.

If nickel oxide be absent a white enamel will be obtained. At the mill 100 parts of Glaze I. with 15 to 25 parts of Glaze II. are taken.

Later, both inventors propose (D. R. P., 186,423), to employ the corresponding amount of strontium or barium phosphate, instead of the calcium compound, since it is thereby possible to add larger quantities of the opaque-producing phosphates, greater lustre being obtained with convenient fusibility and viscosity.

For the preparation of opaque enamels by means of calcium phosphate the process of D. R. P., 166,672, and also the following by Wagner (D. R. P., 179,440), may serve, in which all the calcium phosphate used for the prevention of slag and combustion of the iron surface, as well as for producing opacity, is present at the outset in the enamel. This latter process consists in the use of mixtures of glazes, one of which serves for bringing about turbidity, the other as a glass flux. The expansion coefficients of the glazes employed as mixture components must not differ appreciably from one another. As examples, glazes of the following composition are employed :—

Difficultly Fusible Glass.—Na_2O 16·58, calcium fluoride 5·21, lime 11·23, phosphoric acid 9·49, boric acid 9·36, silica 48·13.

Easily Fusible Glass.—Na_2O 18·03, calcium fluoride 11·33, aluminium fluoride 8·14, boric acid 10·17, silica 52·33.

Four parts of the difficultly fusible glass are mixed with 1 part of the easily fusible variety.

By melting together alkaline phosphates and calcspar the calcium phosphate turbidity is produced according to Amer. Pat., 589,554 (Trainer). A similar enamel is obtained from 32 parts quartz, 20 felspar, 20 sodium phosphate, 20 calcspar, 18 soda, 4 potassium nitrate, 10 fluorspar, 2 clay, 0·005 cobalt oxide. For the same purpose lead phosphate was also at one time proposed.

Knöspel * (D. R. P., 133,943), for the preparation of opaque glazes by means of calcium phosphate, replaces the potassium carbonate, whole or part, by barium compounds (oxide, hydroxide, carbonate, chlorate, nitrate, sulphate, etc.). In this way he obtains a glass which, in the molten state, is malleable and easily moulded, but possesses sufficient rigidity when solid.

The object of D. R. P., 81,754 (Trainer), is sharply contrasted with the above process, since the borax and cryolite are wholly or partially replaced by alkaline phosphates with exclusion of the alkaline earths. Thereby glass fluxes are obtained which are very viscous and elastic, but of sufficient fusibility and lustre. Simultaneously, an opacity is developed in the glaze (aluminium phosphate ?), which is particularly intense if heavy metals are added. In no case may the amount of alkaline phosphate exceed 5 per cent. of the total mass, since otherwise the desired action as flux and turbidity agent will be inhibited, as well as economy. In general the use of phosphates as opaqueing agents cannot be recommended, as such enamels are brittle, readily chip, have a tendency towards blister development, and acquire a dull lustreless appearance.

Zirconium Oxide.—This agent has been proposed at various times for the preparation of opaque glazes and enamels. At present, however, the amount required for the proper effect is still too great and too expensive for it to compete as a substitute with stannic oxide, although such is theoretically possible, since zirconium oxide has been established experimentally as a turbidity-producing agent.

The problem of using zirconium oxide or other zirconium compounds has recently been the subject of detailed investigation by Dr. Ing. August Hartmann.† Hartmann's assertions as to the good opaque qualities of pure zirconium oxide (pre-

* Vondracek, *Sprechsaal*, 1909 (41), pp. 598-599.

† Zirconemail, "Dissertations Arbeit," *Techn. Hochschule*. Münich, 1910.

pared objection-free by new methods by the Chemische Fabrik Wesenfeld, Dicke & Co., of Barmen, and also by the Fabrik Güstrow in Meckl) in the presence of large quantities of cryolite, cannot provisionally be confirmed by the author.* It is questionable whether the extraordinary amounts of cryolite (18 to 21 per cent.) required by Hartmann in the presence of 14 per cent. zirconium oxide will give a durable and reliable enamel. Hartmann gives the following recipe, among others :—

Felspar, ...	37·5 per cent.
Borax, ...	18 ,,
Cryolite, ...	21 ,,
Quartz, ...	10·5 ,,
Saltpetre, ...	0·7 ,,
Zirconium oxide in the melt, . .	8 ,,
Zirconium oxide addition at the mill,	6 ,,
Clay addition at the mill, . .	7 ,,

The greater opacity can in this case be traced essentially to the abnormally high cryolite content (probably by separated alumina remaining in suspension). As a rule, the author found that the opacity action of zirconium oxide, as well as of titanic acid, which is relatively of such a moderate degree, was connected with the presence of alumina in the enamel. A rising alumina content adds to the turbidity effect of this metallic oxide between certain limits. Zirconium is found naturally as zirconium dioxide (ZrO_2) and zirconium silicate ($ZrSiO_4$). The naturally occurring zirconium silicate is always impure, and contains at the most 66 per cent. ZrO_2, while, on the other hand, the zircon oxide found in large quantities in Brazil contains up to 83 per cent. ZrO_2.

The price of this ore is given by Hartmann at 580s. per 1,000 kg. One kg. chemically pure zirconium oxide should cost 2s. to 2s. 6d.

The first patent for the use of zirconium oxide in enamel manufacture was taken out by the firm of Drs. Hillringhaus and Heilmann, in Güstrow (D. R. P., No. 189,364).

Dr. Hartmann has acquired very good results with zirconium oxide in large scale experiments carried out at the enamelling

* Dr. Jul. Grünwald, "Ueber Zirkonoxyd in der Emailindustrie," *Sprechsaal*, No. 5, 1911.

works of Gebr. Baumann at Amberg, which certainly contrast with experience obtained in other ways. The non-poisonous character of zirconium oxide appears to be conclusively established.

The analysis of a zirconium oxide produced by the chemical firm, Wesenfeld, Dicke & Co., of Barmen, gave :—

ZrO_2, ...	99·91 per cent.
TiO_2, ...	0·04 ,,
Fe_2O_3, ...	0·01 ,,
Al_2O_3, ...	0·01 ,,
SiO_2, ...	0·02 ,,
	99·99 ,,

Pure zirconium oxide is alleged to be produced on the large scale by decomposing the crude ore with sodium bisulphate and precipitating the neutralised aqueous solution by aniline sulphate.

According to Dr. Hartmann, zirconium silicate is a much less suitable opacity agent than the pure oxide, and he states that still better results are obtained by the use of zirconium borate, which is added at the mill, similar to stannic oxide. It is doubtful whether the addition of a borate in large amounts at the mill would not give inconvenience when coating, and on this point further experience must be gathered.

In view of the present condition of the zirconium enamel question, practical enamellers are advised to be sceptical and reserved as a protection against the similar disappointments experienced by so many with stannic oxide substitutes.

Zirconium oxide gives a grey to dirty yellowish enamel similar to titanic acid, which is far removed from the rich white appearance of the stannic oxide enamel.

Further, arsenic acid has been recommended for certain artistic enamels. Arsenic enamels are easily recognised by their bluish translucent border. The use of arsenic products cannot be advised, for though it is undeniable that the addition of arsenic acid to an enamel enhances its lustre, yet, on the other hand, its resistance to chemical influences is diminished.

A. Lesmüller has taken out a patent for rendering enamels opaque by means of the oxides of tetravalent elements.

The Opaqueing of Glass and Enamel.—If boric acid compounds,

especially borax or boron trioxide, be melted with the oxides of tetravalent elements—*i.e.*, with the oxides of silicon, tin, lead, titanium, zirconium, or thorium, solution to colourless glass takes place if sufficient amounts of flux be employed. On a large scale solution takes place if silica is also present in addition to the above-named oxides. Such melts of these boric acid glasses saturated with the above tetravalent oxides develop opacity when cooled in a current of steam or acid vapour, which is caused by the separation of a special series of double compounds of boric acid. These substances separate on prolonged cooling as extremely fine amorphous masses, and are distributed uniformly throughout the glassy flux. They are very permanent towards acids and alkalies, being only brought into solution by hydrofluoric acid. For the preparation of such glasses the respective boric acid compound is melted up with one or more of the oxides named in such proportions that a melt is produced saturated with these oxides. During the cooling a current of steam or acid vapour is conducted over the molten mass, and the product obtained is then introduced into the glass or enamel mixture. (D. R. P., 218,316, April 1st, 1909.)

Pulverised porcelain fragments have also been proposed as opacity agents, and introduced on the market under various fantastic names.

A recent product, "Byllonit," put on the market by the Vienna firm, Landau & Co., has been much talked of recently, and its progress will be followed with great interest. Exact information is not yet to hand, although the product appears to contain the oxides of beryllium, zirconium, and cerium, and to be prepared by a complicated process.

X. NICKEL OXIDE.

Since nickel oxide plays a minor part in enamel manufacture, only a brief notice of the otherwise extremely interesting chemical technology of nickel can be given here.

Nickel has long been known, although in the metallic state it is seldom found native, being usually met with in its compounds. The word originates from Swedish mythology (nickel = false Kobald, see *Cobalt*). Cronsted discovered nickel in 1751, and regarded it as a half-metal proceeding from the decomposition of cobalt, while Bergmann first prepared it pure in 1775. Ancient coins of the year 235 B.C. have been found containing 22 to 23 per cent. nickel and 77 to 78 per cent. copper. It was first metallurgically produced on the large scale in 1824 at a nickel works in Gloggnitz, Lower Austria.

Nickel ores are classified in three divisions :—

I. *Nickel Ores containing Arsenic and Antimony—e.g.—*

(*a*) Kupfernickel (arsennickel, niccolite, rotnickelkies), NiAs, with 43·61 per cent. nickel, of which a part is usually replaced by cobalt or iron.

Occurrence.—In the Harz, Freiberg, Schneeberg, Erzgebirge, Schlademig (Austria), Dobschau (Austria), Allemont (France), Chalam in Connecticut (U.S.A.).

(*b*) Weiss nickelkies (chloanthite), $NiAs_2$, with 28·2 per cent. Ni. Tin white in colour. Occurs as above.

(*c*) Antimon nickel or breithauptite, NiSb, with 31·5 per cent. Ni.

(*d*) Nickel antimonglanz or ullmannite ($NiSb_2 + NiAs_2 + NiS_2$), with 26 per cent. Ni.

(*e*) Nickel glance = nickel arsenic glance = Gersdorffite ($NiAs_2 + NiS_2$), with 35 per cent. Ni.

II. *Nickel Ores containing Sulphur and mixed with Iron or Copper Pyrites—*

(*a*) Millerite or Haarkies, NiS, with 64·5 per cent. nickel. Occurrence—Canada, Sweden, etc.

(*b*) Eisen nickelkies, nicopyrites, or Pentlandite (2FeS + NiS), with 18 to 21 per cent. from South Norway.

III. *Nickel Ores containing Oxygen*—

(*a*) Nickel magnesium hydrosilicate (Pimelite, Alipite, Redwanskite, Garnierite). At the present time Garnierite is the most important ore, and was discovered by Garnier in New Caledonia. (MgO, NiO) $SiO_2 + nH_2O$, with 14 to 25 per cent. Ni.

(*b*) Nickelbloom (nickel-ochre, nickel-green, Annabergite), $Ni_2As_2O_8 . 8H_2O$, with 29·5 per cent. Ni. Found in Germany, Erzgebirge, Nowada, Urals, etc.

The winning of the nickel oxide is similar to that of cobalt. Most methods for obtaining nickel start from Garnierite, which is treated on the large scale in the blast furnace and converter similar to iron ores.

Pure nickel oxide is best prepared from chemically pure nickel by solution in nitric acid and subsequent heating to redness of the nickel nitrate obtained.

A detailed description of the nickel manufacture cannot be given here.

The sulphur-containing ore is roasted, whereby the " rohstein " is obtained, which still contains nickel sulphide, and this is smelted in the shaft furnace with coke and appropriate flux. The " nickel matte " so obtained from the reduction being poor in nickel and rich in iron must be further concentrated by repeated roasting and reduction. By the oxidising smelting of the concentrated nickel matte in the reverberatory furnace or converter, and in the presence of silica (for obtaining the iron as slag), the iron is removed.

By roasting the iron-free matte in the reverberatory furnace nickelous oxide (NiO) is obtained.

From nickel ores containing arsenic the nickel oxide is obtained by :—

(1) Working up the ore for crude speiss (containing iron).

(2) Repeatedly roasting and smelting the crude speiss to obtain a nickel speiss poor in iron and rich in nickel.

(3) Converting the nickel speiss from (2) into crude nickel by a process carried out in the following stages :—

Roasting the refined nickel speiss, with addition of substances rich in carbon, in order to produce nickel arsenate. Addition of saltpetre and soda to convert the arsenate into soluble alkaline arsenate, by which there is also formed nickelous oxide, NiO.

Ore.	Synonym.	Chemical Formula.	Colour.	Percentage, Nickel Content.	Place of Occurrence.
Nickelin, . . .	Kupfernickel.	Ni_2As_5.	Copper-red.	44	Saxony, Bohemia.
Chloanthite, . .	Weissnickelkies.	NiAs.	White, metallic.	28	,, Hesse.
Annabergite, . .	Nickel ochre.	$3NiO . As_2O_5 . 8H_2O$.	Greenish.	29·6	,, Bohemia.
Gersdorffite, . .	Nickel glance.	$NiS_2 . NiAs$.	Steel-grey.	31·8	Steiermark, Harz.
Millerite, . . .	Haarkies.	NiS.	Brass-yellow.	61·8	Nassau, North America.
Siegenite, . . .	Linneite.	$(Ni . Co)_3S_4$.	Steel-grey.	22	Musen, Batnaes (Sweden).
Pentlandite, . .	Nicopyrites.	2FeS . NiS.	Bronze-yellow.	18·3	Norway.
Grumanite, . .	Bismuth nickel.	Nickel bismuth sulphide.	Steel-grey.	40	,,
Breithauptite, . .	Antimonal nickel.	NiSb.	Violet, copper-red.	32·6	Harz, Pyrenees.
Ullmannite, . .	Nickel glance.	$Ni_2S_2 . Sb$.	Light steel-grey.	26·1	,,
Genthite, . . .	Nickel gymnite.	$RO(SiO_2)_2 . H_2O$.	Apple-green.	12·6	Urals.
Bunsenite, . .	Seldom occurs.	NiO.	,,	12·6	,,
Texasite, . . .	Zazarite.	$NiO . CO_2 + 2NiO . H_2O + 4H_2O$.	Emerald-green.	51	Texas, Shetlands.
Morenosite, . .	Nicekl vitriol.	$NiSO_4 . 7H_2O$.	Light green.	21	Cap. Ortegal, Hesse.
Pimelite, . . .	Comarite.	Aluminium nickel silicate.	Green.	15-20	Frankenstein (Silesia), Saxony.
White pyrites, . .	..	,, ,,	Grey-white.	15-20	Steiermark.
Garnierite, . .	Numeaite.	$(MgO, NiO)SiO_3 . nH_2O$.	Green.	14-25	New Caledonia.

The Metallurgy of Nickel Ores containing Oxygen, and especially of Garnierite.*—Garnierite, as already stated, is a nickel-magnesium hydrosilicate. Formerly these ores were smelted at Kumea, in New Caledonia, with coke and other additions, in the blast furnace, to form an iron-nickel alloy, which is subsequently refined in Europe by oxidising smelting processes. At the present time these New Caledonian ores are sent to Europe in the crude condition. In England, France, and Germany the ores are smelted in the shaft furnace, with sulphur-containing additions, to form nickel matte, which is then refined and roasted to produce crude nickel, as above described.

The crude ores contain :—

6 to 8 per cent. Ni,
10 to 12 per cent. Fe_2O_3,
40 to 45 per cent. SiO_2,
6 to 9 per cent. MgO,
3 to 4 per cent. Al_2O_3,
12 to 15 per cent. water.

The sulphur-containing additions which are made to the blast furnace are the residues from the soda manufacture (which see), consisting principally of calcium sulphide (CaS). The latter reacts with the nickel silicate of the ore, forming nickel sulphide and calcium silicate. Gypsum is reduced in the furnace by coke to form calcium sulphide, and acts in the same way as the calcium sulphide of the soda residues.

In a blast furnace 5 m. high 30 tons of ores are worked up in twenty-four hours.

At Frankenstein, in Silesia, ores similar to Pimelite are found with 2·5 to 3·5 per cent. nickel content, and here a vigorous industry has sprung up.

The use of nickel oxide in enamel manufacture is limited to the replacement of cobalt oxide in many ground enamels (see *Cobalt oxide*). One can purchase green nickel oxide—*i.e.*, nickelous oxide, NiO, with 78·5 per cent. nickel content, and grey-black nickel oxide, Ni_2O_3, with 70·9 per cent. Ni.

In a later chapter (see *Cobalt oxide*) it is shown that many enamelling firms use nickel oxide for ground enamels. At all events, the lesson of practice is that, with proper care, nickel oxide may be employed, although it is impossible to replace

* A. Rzehulka, "Der Gegenwärtige Stand der Nickelwinnung."

cobalt oxide entirely. For large articles a ground enamel is often used in which the cobalt oxide has been replaced, wholly or partly, by nickel oxide, and although such a ground enamel may be fairly trustworthy, the durability is not so good. A truly excellent ground enamel may only be prepared with cobalt oxide, and the industry has not been advanced by the contrary assertions of less competent enamellers, who generally have only been engaged for a short term of years in a small works. If a nickel ground must be used with care, much more so must one free from cobalt and nickel oxides—*i.e.*, the so-called "white-ground," and this should be banned in enamel works, since value depends upon a uniformly good and certain quality.

In cases, however, where nickel oxide is employed for ground enamels, a larger quantity is recommended than is proposed for cobalt oxide in the original recipe.* This, however, is of less consequence, since nickel oxide is relatively much cheaper.

* See the author's *Theory and Practice of Enamelling on Iron and Steel.* C. Griffin & Co., London, 1909.

XI. COBALT OXIDE AND COBALT COMPOUNDS.

Cobalt compounds, especially the oxides, furnish the ceramic industry with their most valuable and indispensable pigments for the preparation of dark to light blue colours, or, when intimately mixed with chromium oxide for greenish-blue shades.

As a rule, the enameller is frequently ignorant of the chemical technology of this exceedingly interesting body. Metallic cobalt in contrast to nickel has extremely insignificant technical utility, although its compounds are indispensable to the ceramic industry.

The word cobalt originates from Swedish mythology. The mountaineers, searching for precious minerals in the Middle Ages, were disappointed if they mined cobalt or nickel ores instead of silver, and ascribed their mishap to an evil spirit—viz., "Kobold," or "Nickel." The terms "Kobold" and "Bosnickel" have still a similar meaning at the present time in German idiom.

Metallic cobalt was isolated for the first time by the Swedish chemist, Brandt, in 1733, and is obtained pure by heating cobaltous oxide (CaO) with carbon to redness, or in a current of hydrogen. It is a reddish-white metal, very tough, and difficultly fusible. (According to recent determinations by Gürtler and Tammann cobalt melts at 1,528° C.) Its specific gravity is 8·5—*i.e.*, it is heavier than iron, and is feebly magnetic. Cobalt remains unaltered in air or water; hydrochloric and sulphuric acids attack it with difficulty, while nitric acid, on the contrary, easily dissolves it to form cobalt nitrate [$Co(NO_3)_2$].

The most important compounds are derived from cobaltous oxide, the cobaltic derivatives being much less stable.

The most important cobaltous compounds are :—

Cobaltous Chloride, ($CoCl_2$), which is obtained by solution of cobaltous oxide in hydrochloric acid.

Cobaltous Hydroxide, $Co(OH)_2$, obtained by precipitating hot solutions of cobaltous salts with alkalies.

Cobalt Sulphate, $CoSO_4 . 7H_2O$.—Dark red monoclinic crystals.

Cobalt Nitrate, $Co(NO_3)_2 . 6H_2O$.—Red crystals deliquescent in air.

Cobalt Silicate or *Smalt*.—An important blue pigment obtained

Table giving the most Important Cobalt Minerals and their Chemical Composition.

Name.	Chemical Formula.	Composition.	Colour.	Percentage, Cobalt Content.	Place of Occurrence.
Speiss cobalt = Smaltine,	$CoAs_2$.	28·12 % cobalt. 71·88 % arsenic.	Steel-grey.	28·12	Schneeberg, Freiberg, Annaberg, Joachimsthal, Allemont.
Cobalt glance = Cobaltine,	CoAsS.	35·41 % cobalt. 19·33 % sulphur. 45·26 % arsenic.	Reddish-silvery-white, metallic.	35·41	Tunaberg, Vena, Skutterud.
Tesseralkies = Skutterudite,	$CoAs_3$.	20·68 % cobalt. 79·32 % arsenic.	Tin-white to lead-grey.	20·68	Skutterud, in Norway, Crête d'Omberenza.
Cobalt bloom = Erythrite,	$(AsO_4)_2CO_3 + 8H_2O$.	37·47 % cobaltous oxide. 38·46 % arsenic acid. 24·07 % water.	cherry-red.	20	Skutterud, Allemont.
Cobalt manganese ore = Asbolan,	$CoO \cdot 2MnO_2 + 4H_2O$.	20 % cobaltous oxide. 21 % water.	Black.	Fluctuating.	Kamsdorf, Saalfeld, etc.
Cobalt nickel pyrites = Cobaltkies,	R_3S_4. R = Co and Ni.	Fluctuating.	,,	,,	Freiberg, Bastnaes.
Arsenkupfer, . .	$(CuNiCo)_3As$.	,,	,,	,,	Chili, Zwickau.
Cobalt-arseno pyrites, .	(FeCo)AsS.	,,	,,	,,	Norway.
Cobaltspar, . . .	$CoCO_3$.	63 % CoO. 37 % CO_2.	,,	,,	Schneeberg.

by fusing cobalt ores with potash and quartz, whereby the cobalt forms a silicate (smalt) with the silica, while the other metals accompanying the cobalt in its ores, such as bismuth, arsenic, and nickel, separate as a fused " regulus " (termed cobalt speiss), from which nickel is prepared. For further details, see *Manufacture of Smalt.* The cobaltic oxide, Co_2O_3, passes at a red heat into cobalto-cobaltic oxide, Co_3O_4 . (Co_2O_3 . CoO).

Cobaltic Hydroxide, $Co(OH)_3$, separates as a dark brown powder, when a stream of chlorine is passed through a solution of a cobaltous salt made alkaline with caustic soda. Details will follow later.

Cobalt salts are not poisonous.

Before entering into a brief description of the metallurgy of cobalt, the most important cobalt ores will be reviewed, among which number are cobalt glance and speiss cobalt.

Cobalt Glance, or cobaltite, crystallises in the regular system and exhibits cleavage. Hardness = 5·5, specific gravity 6 to 6·3. It possesses metallic lustre, and is silver-white inclined to red in colour, though it often occurs as a steel-grey variety with a violet tinge or greyish-black when containing much iron. The streak is greyish-black. Cobalt glance is a sulpharsenide of cobalt of formula CoAsS.

Chemical Composition.

	Average.	Maximum Cobalt Content.	Minimum Cobalt Content.
	Per cent.	Per cent.	Per cent.
Cobalt, ...	28·90	39·0	18·5
Iron, ...	8·50	2·0	16·3
Arsenic, ...	42·30	34·7	45·0
Sulphur, ...	20·04	21·7	19·1

The most important sources are in the ore deposits of the crystalline schists, frequently accompanied by copper pyrites at Tunaberg, Vena, Riddarhytta in Sweden, and Skutterud in Norway. In the mica schists of Auerbach in Silesia, in the ores at Siegen, and at Daschkessan, near Elisabethpol, in the Caucasus (a deposit 2 feet thick). This is the richest ore for the blue pigment manufacture.

Speiss Cobalt or Smaltine.—Crystallises in the regular system, but is mostly found in massive, grape-like, or other reticulated

shapes. It is brittle, has a hardness of 5·5, a specific gravity of 6·37 to 7·3, and is tin-white to light steel-grey in colour, although frequently tarnished red by transformation into cobalt bloom.

The chemical composition is $CoAs_2$, containing 28·12 per cent. cobalt and 71·88 per cent. arsenic.

The average composition, however, is :—

Cobalt,	25·0 per cent.	Iron,	5·1 per cent.
Nickel,	5·4 ,,	Arsenic,	64·5 ,,

The sources are the so-called cobalt veins of the Erzgebirge, together with silver ores, bismuth, etc., at Schneeberg in Saxony (a part of the speiss-cobalt found there is chloanthite or Weiss-nickelkies and arsennickelkies, $NiAs_2$); also at Marienberg, Annaberg, and Johanngeorgenstadt ; at Rügen, in the Kupfer-schiefer at Riechelsdorf and Bieber ; with spathic iron and copper ores at Schladming and Döbschau in Hungary ; also at Wittichen, Allemont, Cornwall, and La Motte (Missouri).

After cobalt glance, the most important cobalt ore is speiss-cobalt, and recently rich ores have been discovered in New Caledonia.

Caledonian Cobalt Ores.—Hitherto two varieties of such minerals have been recognised, each containing manganese ; one is termed " truffe " by the Caledonian smelters because of its truffle-like structure, the other, which is without structure and of more frequent occurrence, has an average content of 5 per cent. cobalt oxide.

According to E. Capelle's analysis, the Caledonian cobalt ores contain :—

Insoluble matter (partly consisting of chrome-iron ore),	4·593 per cent.
Loss at red heat,	25·600 ,,
Ferrous oxide (FeO),	14·531 ,,
Alumina (Al_2O_3),	27·549 ,,
Lime (CaO),	1·400 ,,
Magnesia (MgO),	0·956 ,,
Manganese oxide (Mn_2O_3),	13·658 ,,
Cobalt oxide (Co_2O_3),	4·519 ,,
Nickel oxide (Ni_2O_3),	2·691 ,,
Excess oxygen,	4·313 ,,
	99·810 ,,
Cobalt calculated as metal,	3·558 ,,

According to Prof. Carnot, the ores from Koé and Canala contain :—

		Koé.		Canala.	
		I.	II.	I.	II.
		Per cent.	Per cent.	Per cent.	Per cent.
Silica, ...	SiO_2	8·40	8·00	4·50	31·00
Iron oxide + alumina, .	$Fe_2O_3 + Al_2O_3$	18·40	39·00	39·33	40·60
Manganese oxide, . .	Mn_2O_3	20·20	18·60	18·60	10·60
Cobalt oxide, . . .	Co_2O_3	21·10	8·70	14·50	10·60
Magnesia, . . .	MgO	6·20	2·10	traces	0·60
Loss at red heat, . .	..	25·60	24·00	23·30	11·00
Metallic cobalt (calculated),	..	15·80	6·51	10·11	4·27

Naturally, these Caledonian ores must be properly sorted before working up, since the cobalt content seldom exceeds 10 to 15 per cent., and on an average only 5 per cent. may be taken. It is rather unusual that in the above analyses no mention is made of nickel, the inseparable companion of cobalt.

A. M. Villon * found the following composition :—

		I.	II.
		Per cent.	Per cent.
Loss at red heat, ...	..	25·415	25·120
Iron oxide + alumina, . . .	$Fe_2O_3 + Al_2O_3$	41·122	38·920
Lime + magnesia, ...	$CaO + MgO$	2·111	0·800
Manganese oxide, ...	Mn_2O_3	15·311	20·190
Cobalt oxide, ...	Co_2O_3	4·502	5·135
Nickel oxide, ...	Ni_2O_3	2·144	3·155
Silica, ...	SiO_2	8·712	6·545

Production of Smalt and Cobalt Oxide—I. Smalt Manufacture— (*a*) *The Chinese Method.*†—In the Chinese glass works at Canton the so-called lam-o-li-shek—*i.e.*, "stone for blue glass"—is employed for the production of a blue colour in glass and porcelain. It appears as if the Chinese are unaware how to produce colourless glass. They purchase glass fragments from Europe and America, which they classify according to colour and quality, and then melt in pots, 67 cm. high, having a lower diameter of 40 cm., and an upper one of 11 cm. One or two of these pots are placed in a rectangular furnace of primitive character, which is heated with anthracite, for which purpose from 150 to 200 kg.

* *Encyclop. Chim. Nickel et Cobalt*, Tome v.

† Thos Id. Bowler, *Chemical News*, 31st Aug., 1888.

anthracite per pot are required. The blowpipe is very short and wide, while the moulds are made of clay and dust. It is astonishing how the Chinese, by means of their small apparatus, are able to separate the cobalt from the iron, manganese, and nickel, even when the cobalt content in the ore does not exceed 2 to 4 per cent.

The crude cobalt mineral is first carefully washed, and every single piece of it scrubbed with a brush, in order to remove the adhering clay which contains iron. The ore is next dried and pulverised to a fine powder, which is afterwards ground in a hand mill with water. The whole mixture is then conveyed to a vessel, in which it is vigorously stirred until evening, and then allowed to settle overnight. On the following day the water is drained off, taking with it the uppermost layer of the settled powder. The latter consists of the specifically lighter earthy substances, while the residual mass is made up of the oxides of iron, manganese, nickel, and cobalt. This mass is removed, mixed with a small quantity of borax, and placed in one of the above-mentioned pots containing the glass. The melting is now carried out, and during the first twelve hours the mass so fused acquires a dirty greenish-black colour. By degrees this mixed colour is transformed into a bright bluish-violet similar to amethyst. It appears as if the iron and nickel are completely reduced, for after 36 to 40 hours' heating scarcely any of the iron or manganese colour can be detected in the mixture.

The lowest portion of the fused glass in the pot is rejected as worthless. (This part probably contains the total impurities of iron, nickel, manganese, etc.)

For the purpose of porcelain painting, the Chinese frit the same mineral with felspar, kaolin, and much borax. This frit is ground to fine powder, and employed for painting on the biscuit. The Canton process is as follows :—

The manipulator takes the burnt biscuit and covers this with a glaze consisting of borax, felspar, and clay, which, when sufficiently dry, he paints upon, and in one single operation burns in both the enamel and the colour.

A sample of the cobalt mineral gave the following composition :—

Iron oxide,	35·00 per cent.	Cobalt oxide,	3·50 per cent.
Manganese oxide,	13·10 ,,	Gangue,	46·00 ,,
Nickel oxide,	3·50 ,,		

The gangue consisted for the most part of silica and aluminium silicate.

The cobalt mineral is found at the foot of a chain of sandhills in the neighbourhood of the town of Msang-Sheng. The geological formation probably corresponds to the Upper Cambrian.

(*b*) *The Saxony Method of Smalt Preparation.*—Glass coloured with cobalt has been known for a long time in China. In Europe, however, it was first discovered about 1540. A Nuremberg glass-maker, named Schürer, appears to have been the first to try melting cobalt ore, termed "Kobold," with glass about 1540, and he acquired, much to his astonishment, a beautiful blue colour thereby. Soon this news spread abroad, and the Dutch seized upon this invention to produce blue glazes, which they used in the pulverised state for colouring glass and decorating pottery.

In Saxony the preparation of smalt is made as follows :— The mineral is first splintered, then carefully sorted and washed. This product is called the "Schlich," and is roasted in a rotatory furnace. Above the furnace are chambers for condensing the vapours of arsenic oxide evolved during roasting. If the ore is poor in nickel, it is completely roasted, while in the contrary case the roasting is only taken so far that the nickel is not oxidised to nickel oxide, but remains behind as nickel arsenide. The roasting at the same time converts the cobalt into oxide. During the operation the oxide is raked from time to time. The manufacture is usually associated with that of arsenic oxide whenever the cobalt ores contain arsenic, the latter being deposited in the above-mentioned chambers (poison traps). The roasting itself lasts 10 to 12 hours, after which the mass is withdrawn from the furnace, allowed to cool, finely ground, and passed through a silken sieve. This powder is called "Zaffer" or "Saffler."

About 30 cubic metres of wood are required per 600 kg. roasted ore (Schlich), and as a by-product 25 per cent. of arsenic oxide is obtained.

The Schlich is mixed with sand and potash in amounts depending on the character of the cobalt mineral (in general 3 parts ore and sand to 1 part pure potash)—*e.g.*, the ore for the preparation of an ordinary smalt of average excellence is mixed in the proportion :—

Roasted Schlich, ...	25 parts.
Mixture of Schlich and roasted sand, containing cobalt, ...	20 ,,
Sand, ...	200 ,,
Aeschel (the finest pale blue glass powder),	35 ,,
Potash, ...	100 ,,

A smalt of a pure azure-blue colour is obtained from—

I*a*. Schlich, ...	20 parts.
Sand, ...	50 ,,
Aeschel, ...	20 ,,
Potash, ...	40 ,,

The purer the materials employed for smalt preparation are, the more beautiful the product.

Crushed quartz is used for sand, after first being heated to redness in a lime kiln, crushed moist, then well washed with water, dried, and finally heated to redness in a furnace close to that for the glass melting.

The Saxony furnaces have a conical form with elliptical cross-section, $3 \times 1{\cdot}30$ m. at the base and $4 \times 2{\cdot}20$ m. above. Under the furnace is a fire-box, 1 m. deep, charged with wood, over which is a packed mass of large pieces of quartz. 700 cwts. of quartz are taken per furnace charge, and the firing, which lasts 36 hours, requires 80 cubic metres of wood.

The fritted mass is now placed in a melting pot and taken to the ordinary glass furnace. During the melting it is frequently stirred, and samples are taken from time to time to ascertain whether the mass is uniformly melted and coloured. The whole is then allowed to flow into water, and thereby splintered. Sometimes, beneath the blue glass in the melting pot, the so-called cobalt speiss is found—*i.e.*, those substances which do not volatilise on roasting, have not been separated by washing, and, being specifically heavier, have separated from the entire mass and settled to the bottom. This speiss is removed before withdrawal of the glass, either through an opening made at the base of the pot, or else carefully ladled out. The glass (smalt) prepared according to the above-described method, is now dried and finely powdered. The ground glass or smalt (from *smeltan*, which is the old High German for *schmelzen—i.e.*, the melt—and was earlier termed *Schmalte* or blue pigment) is placed in a vat

full of water, and vigorously stirred, after which it is allowed to stand for half-an-hour, whereby the coarser parts (known as *Streublau*) settle, and are subsequently ground up again.

The turbid-coloured water is then poured into a second vat, in which the pigment proper (also termed *Couleur*) settles to the bottom.

After twenty-four hours the turbid water is decanted from the second vat into a third, in which it remains until quite clear, when the finest and palest glass powder termed *Aeschel* settles out. The pigment, and also the *Aeschel*, is next washed two to three times, and the wash waters which carry with them the finest portions of the glass powder are intercepted in filters. By this means the finest *Aeschel*, which is only feebly tinted, is retained. The residual pigments in the various settling tanks, after running off the water, are dug out, triturated, dried, sieved, packed into barrels, and then placed on the market.

The smalt is classified according to its degree of fineness into coarse blue (*Streublau*), pigment, and *Aeschel*, the first being denoted in the trade by H, the second by C, and the last by E.

Respecting the intensity of the colour, each sort is distinguished as fine, middle, and ordinary by the letters F, M, and O. In the first class, colours of varying degrees of fineness are denoted by the letters F, F F, F F F, F F F F, expressing fine, two-fold, three-fold, and four-fold respectively.

More intense than the last, which is termed "Azure," or "King's Blue," do not occur.

List of the Smalt Brands to be found on the Market.

H, ...	Ordinary smalt.
E, ...	Aeschel.
B, ...	Bohemian smalt.
C F, ...	Ground pigment.
F C, ...	Fine pigment.
F C B, ...	Fine Bohemian pigment.
F C, ...	Finer Aeschel.
M C, ...	Average.
M C B, ...	Average Bohemian.
M E, ...	Average Aeschel.
O C, ...	Ordinary pigment.
O C B, ...	Ordinary Bohemian pigment.
O E, ...	Ordinary Aeschel.

One speaks of azure blue, smalt blue, zaffer blue, Saxon blue, enamel blue, cobalt blue, etc.

The following are analyses of some varieties of smalt :—

SURVEY OF THE PERCENTAGE COMPOSITION OF SOME TYPICAL SMALTS.

Component.	Norwegian Smalt.		German Smalt.			French Smalt.				
	Dark.	Dark Aeschel	Pale.	Coarse Blue.	Pig-ment, C.	I.	II.	III.	IV.	V.
Silica, .	70·86	66·20	72·11	72·21	70·11	75	70	65	63	60
Cobalt oxide,	6·49	6·75	1·95	20·54	21·58	20	26	30	30	30
Potash, .	21·41	16·31	1·80	6·75	7·20	2	3	5	7	10
Alumina,	0·43	8·64	20·04	0·22	0·11	..	..	..	..	..
Arsenious acid,	..	..	..	..	..	1	1	1	1	1

Finally, there still exists a French method of smalt preparation, which consists in melting together cobalt oxide direct with quartz and potash. In this way an absolutely first-class product of desired intensity can be prepared, although the process is correspondingly more expensive.

The quartz is heated to redness and ground as in earlier methods. The materials are then intimately mixed and melted in the crucible. Further treatment is analogous to that of former methods, only instead of cobalt speiss pure cobalt oxide is here employed. The smalt so obtained is very pure, and more durable than the ordinary product.

2. The Production of Cobalt Oxide.—(*a*) By degrees the use of smalt for ceramic pigments is declining, since it is difficult to acquire continuously the same quality of colour intensity in consequence of the fluctuating composition of the ores. In addition, as we have seen, the smalt manufacture is not particularly a simple process.

The preparation of cobalt oxide from minerals consists in first sorting the ore according to value, and then breaking it up into pieces of about 3 cm. diameter. These are then roasted in a rotatory furnace, which allows the evolved arsenious oxide to be trapped and recovered. At the first roasting about 15 per

cent. of the arsenic present in the mineral is evolved. After cooling, the ore is dug out and again roasted, when a further 5 per cent. of the arsenic is removed. In this way about 80 parts of roasted product are obtained from 100 parts of mineral. Recently, oxidation by means of compressed air has been attempted in a specially constructed furnace. The roasted material is fused with 20 per cent. of added quartz in a tank furnace.

The cobalt speiss obtained is vigorously roasted once again in the presence of saltpetre. From the latter, oxygen is evolved, which facilitates oxidation of the cobalt to oxide. It is more advantageous, however, to melt the cobalt speiss in a converter, similar to a Bessemer converter, and provided with an air blast. The process is quite analogous to the Bessemerisation of iron. The speiss obtained is ground, treated with hydrochloric acid, and into the solution thereby formed, gaseous sulphur dioxide is conducted in order to reduce and precipitate the arsenic and copper compounds. After filtration the solution is oxidised by bleaching powder (the chlorine evolved acting as an oxidising agent), or by means of chlorine water (prepared by passing the chlorine evolved by the action of hydrochloric acid on pyrolusite into water). The ferrous oxide present is thereby oxidised to ferric chloride, which is then precipitated as ferric hydroxide by the addition of milk of lime.

The solution separated from the ferric hydroxide precipitate has recently been treated with chlorine or bleaching powder, in order to oxidise the cobaltous chloride. After addition of the calculated amount of soda solution the cobalt is precipitated as cobaltous carbonate. The precipitate is then dried and moderately heated. The well-washed cobalt oxide obtained from the latter still contains nickel oxide, its composition being—

96 per cent. cobalt oxide,
3 per cent. nickel oxide,
1 per cent. iron oxide.

The whole is dried and moderately heated.

Absolutely pure cobalt oxide is more difficult to prepare, and frequently the method is adopted of dissolving pure metallic cobalt in nitric acid, filtering, evaporating to dryness, and heating the cobalt nitrate to redness.

The difficulty of removing the last trace of nickel oxide from the cobalt oxide accounts for the extraordinary difference in price between 100 and 96 per cent. cobalt oxide, and this price difference is sufficiently high to make the 96 per cent. cobalt oxide suffice for most ceramic purposes. Chemically-pure cobalt oxide is, therefore, only used for the choicest porcelain colours. The quite pure oxide has, in consequence, a very restricted use.

(*b*) *Production of Cobalt Oxide from the Residues of Chlorine Works employing Pyrolusite and Hydrochloric Acid.*—In the preparation of chlorine, pyrolusite (manganese peroxide, MnO_2, *q.v.*), and hydrochloric acid react according to the equation :—

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The residue (termed the Weldon mud) consists of manganous chloride and other compounds, due to the fact that manganese ores often contain a little cobalt, as shown by the following composition of a French variety of pyrolusite from Dordogne :—

Pyrolusite, . . .	MnO_2, . .	58·0 per cent.
Iron oxide + alumina, .	$Fe_2O_3 + Al_2O_3$,	12·8 ,,
Cobalt oxide, . .	Co_2O_3, . .	2·0 ,,
Barium oxide, . .	BaO, . .	2·0 ,,
Copper oxide, . .	CuO, . .	0·2 ,,
Hygroscopic water, .	H_2O, . .	5·0 ,,
Chemically bound water,	H_2O, . .	10·0 ,,
Insoluble residue, . .	. . .	10·0 ,,

The cobalt oxide is recovered from the residue by neutralising the hydrochloric acid liquor remaining after the evolution of the chlorine (see above) with finely-powdered chalk. The carbon dioxide evolved completely precipitates the ferrous chloride present as hydroxide, which is filtered through a filter press. The solution is acidified with a little hydrochloric acid and gaseous sulphur dioxide conducted through it, to precipitate the dissolved copper as cuprous chloride, Cu_2Cl_2, which is removed by a further filtration. The filtrate is again neutralised by means of milk of lime, and the dissolved cobaltous chloride precipitated by calcium sulphide. The cobalt sulphide formed is collected at the filter press, washed with water which has been feebly acidified with

hydrochloric acid in order to remove traces of manganese sulphide, then dried and heated to redness in the air, the cobalt sulphide being thus converted into cobalt oxide. From the last filtrate, after removal of the cobalt sulphide which now consists almost entirely of manganous chloride, the pyrolusite is recovered by the Weldon process.

3. Extraction of Cobalt Oxide from the Caledonian Cobalt Ores (see beginning of chapter)—(*a*) *Carnot's Method.**—The Caledonian cobalt and nickel ores are entering more and more into competition with European ores (which contain arsenic), and in consequence have contributed not a little to the fall in price of recent years.

The Caledonian ore is calcined in a shaft or rotatory furnace, to render the clay and iron oxide therein more resistant towards acids, while the oxides of manganese and cobalt still retain their ready solubility. By calcination about one-fourth of the actual mineral weight is removed. The roasted mass is coarsely splintered and treated with its own weight of hydrochloric acid (75 to 80 litres per 100 kg. mineral), either in stone vats or in lead-lined troughs. The whole is maintained some time at 75° C. with evolution of chlorine, and then diluted with cold water accompanied by stirring (using wooden rods). Neutralisation is effected by the gradual addition of powdered calcium carbonate until no further effervescence takes place. After standing some time the whole is filtered through linen filters, and the residue washed to remove the last traces of the dissolved cobalt salts. The residual matter consists of earthy and clayey gangue, iron hydroxide, manganese oxide, and the excess chalk. The rose-coloured solution free from iron contains almost the whole of the cobalt and some manganese. By the careful addition of small quantities of milk of lime, accompanied by vigorous stirring with suitable settling periods, the cobalt can be almost completely separated, since it is the first to be precipitated. The manganese only comes down after an interval. For testing this, a piece of filter paper is dipped from time to time in the solution and then withdrawn ; so long as the paper presents no rose-coloured appearance the cobalt is not all precipitated, but immediately the rose-colour develops the point has been attained at which only manganese is in solution. The precipitated cobalt hydroxide is collected, washed, and dried. If quite pure cobalt oxide be desired, the last traces of manganese

* *Moniteur de la Nouvelle-Calédonie*, Nov. 8th, 1880.

are removed by fusing the precipitate obtained as above with soda and saltpetre, and extracting the melt with water, whereby only sodium manganate and the excess of soda pass into solution. The undissolved portion remaining behind is washed and dried. Carnot's process has been condemned in many quarters, since the separation of cobalt from nickel and manganese by milk of lime is incomplete.

(*b*) *Readman's Method* (1882) *by means of Sulphuric Acid and Glauber's Salt.*—The mineral ground as fine as possible is mixed with anhydrous sodium sulphate (Glauber's salt, Na_2SO_4), (84 parts to 100 parts mineral), and then 65 parts of sulphuric acid are added, a quantity which serves to convert the sulphate into bisulphate. The whole is heated in a reverberatory furnace, stirring with iron bars until the cobalt, nickel, and manganese are transformed into their soluble sulphates, samples being tested from time to time. The excess acid is neutralised by the addition of a fused, finely-ground product, such as lime, aluminium hydroxide, or even bauxite.

The heating is continued for some time, and the mass then withdrawn and splintered, the pieces being systematically treated with hot water to dissolve the sulphates of cobalt, nickel, manganese, and iron. To the clear solution, sodium sulphide (Na_2S) is added, whereby all the cobalt and nickel, as well as part of the manganese, are precipitated as sulphides (1). As soon as the addition of sodium sulphide has proceeded so far that to a sample of the solution only a white precipitate ensues at the most, the transformation into sulphide is at an end. The latter is filtered, and from the filtrate the Glauber's salt is recovered by evaporation and crystallisation. The mother liquor, in addition to the Glauber's salt, contains almost the whole of the manganese. The latter is removed by evaporating the mother liquor and mixing the residue with half its weight of sawdust or coal, and then burning it in the muffle furnace. After cooling, the mass is washed with warm water to dissolve and recover the sodium sulphide formed. The latter then serves again for precipitating the cobalt and nickel. The residue, consisting of manganese sulphide, is converted into oxide by roasting in the furnace.

The cobalt and nickel (in I.) are then separated in the usual way.

(*c*) *Clarke's Method at Glasgow.*—Clarke treats the mineral with ferrous chloride, whereby the iron is converted into the

oxide, and the cobalt, nickel, and manganese into chlorides. The latter are dissolved and precipitated with calcium sulphide, whereby the manganese remains insoluble.

(*d*) *Dickson and Ratte's Method* (*French Pat., Sept. 5th*, 1885).—According to this method the cobalt, nickel, and manganese of the cobalt mineral are dissolved in sulphurous acid, alone, or mixed with a still cheaper acid. The iron oxide remains insoluble. The finely-ground cobalt mineral is levigated with water at 50° C. in vats provided with stirring arrangements, and the sulphurous acid introduced through an upper opening. The whole is then brought into a second vat, whereby the iron oxide and impurities settle to the bottom. The solution is then filtered over a bed of pulverised mineral, which retains the suspended impurities and the excess acid, while the last traces of iron are precipitated. From this solution the cobalt and nickel are precipitated as sulphides by sodium sulphide and separated as already described.

(*e*) *Herrenschmidt's Process, Jan. 14th*, 1888.—The mineral is dissolved in acid, and the cobalt and nickel precipitated as sulphides by means of sodium sulphide. Originally Herrenschmidt recommended a solution of iron sulphate for dissolving the cobalt and nickel, and he has repeatedly altered his process from time to time.

H. Howe, W. Campbell, etc., in the *Transactions of the Am. Min. Eng.*, pp. 53-61 (1907), give some new localities for natural cobalt compounds, and also some new methods for working up cobalt ores, as practised in Ontario (Canada).

The Use of Cobalt Oxide and Cobalt Compounds in Enamel Manufacture.—Smalt is only used at the present time in a few enamel works for the blue colouring of enamels. For this purpose the oxy-compounds of cobalt play an important part during the mixing of ground and blue enamels, and for blues and special bluish-green pigments in the ceramic industry. The market value of cobalt oxide is expressed on the percentages of metallic cobalt which the respective brands contain, and can be very fluctuating, corresponding to the many varieties of oxide or other compounds of cobalt. The price of the product has fallen during recent years, since the discovery of valuable deposits of cobalt ores in New Caledonia and Canada. The following table gives a list of the customary brands, with their cobalt content :—

Brand.	Special Designation.	Chemical Formula.	Percentage, Cobalt Content.
F F Ko,	Finest cobalt oxide. (Superior oxide.)	CoO.	78 per cent.
G K O,	Grey cobalt oxide, I*a*.	CoO.	76 ,,
F K O,	Grey cobalt oxide.	CoO.	75 ,,
R K O,	Black cobalt oxide, I*a*.	Co_2O_3.	70 ,,
S K O,	Black cobalt oxide.	Co_3O_4.	66 ,,
A K O,	Cobalt arsenate.	$Co_3As_2O_8 . 8H_2O$.	29 ,,
K O H,	Cobalt carbonate.	$CoCO_3$.	50 ,,
P K O,	Cobalt phosphate,	$Co_3(PO_4)_2 . 8H_2O$.	34 ,,

The purest brands of cobaltous oxide have a greyish-green colour. According to the method of heating cobalt nitrate [$Co(NO_3)_2$], for example, there is first obtained a black cobalt oxide, which at a red heat becomes the cobaltous-cobaltic oxide (Co_3O_4), and, finally, at a white heat passes into the most valuable oxide—viz., cobaltous oxide—since this possesses the greatest cobalt content. Moreover, the cobaltous compounds are more stable in air and at high temperatures than the cobaltic.

Cobaltous carbonate, $CoCO_3$, is obtained by treating a dissolved cobalt salt with a soda or potash solution, whereby a basic carbonate is precipitated, generally of the formula $2[CoCO_3 + Co(OH)_2] + 5H_2O$. The trade mark is KOH, and it has a rose colour.

Cobalt phosphate is prepared by precipitating cobalt acetate with sodium phosphate :—

$$3(C_2H_3O_2)Co + 2Na_3PO_4 + 8H_2O = Co_3(PO_4)_2 + 8H_2O + 6Na(C_2H_3O_2).$$

Both salts are only important for the pigment industry.

Diverging opinions and hypotheses rule in enamelling circles concerning the use of cobalt oxide for ground enamels, and its influence upon their physical properties. Dr. Vondracek * seeks to explain the action, by assuming that at the firing temperature of the ground enamel the iron is oxidised at the expense of the cobalt oxide or silicate, which oxide, or better, the silicate, is reduced to a lower state of oxidation or even to the metal. The polished iron surface should thereby be attacked and the enamel more intimately united to the metal, whereby the danger of the enamel coat chipping off is reduced.

Tootmann † assumes that a chemical action takes place

* *Sprechsaal*, 1909, No. 14, p. 201.

† *Keramische Rundschau*, 1909 (No. 3), p. 47.

between the ground enamel and the sheet-iron surface, and this for the following reasons :—*

"The ground mixed only with cobalt oxide assumes a blue colour on melting. If the heating be interrupted at this instant, the enamel does not sufficiently adhere, although it is already fused to a complete vitreous condition. In consequence, the firing is continued until the colour turns to black. How then is this colour change, which is essential for adherence, to be explained? I can only assume that the iron forming the substratum for the ground enamel has received some degree of oxidation. For this purpose, however, oxygen is requisite, and may have come from the air of the muffle, although a part may have been given up by the cobalt oxide in its reduction to metal. This metallic cobalt, formed in small quantities and in a very fine state of division, could perhaps form an alloy of porous character with iron on the sheet-metal surface, which would promote a firm adherence of the ground enamel, while the cobalt separated out of the silicate flux would be replaced by iron. With a colourless ground there actually occurs a slight colour change, so that an oxidation of iron by the air is scarcely probable. The possibility that a similar action to that indicated really takes place is, therefore, extremely likely. At all events, there is only the alternative that such or similar processes occur, and the problem needs more detailed investigation. It might perhaps be assumed that by the action of boron upon iron (see above) chipping may be promoted, and that the cobalt oxide prevents or retards in some way the formation of such a compound."

In another communication † Vondracek defines a ground enamel as a colourless enamel which contains an addition of cobalt or nickel oxide. "These oxides increase the adherence of the enamel, as experience has testified. How this peculiar action of the oxide arises is very hard to say, although very good adhering ground enamels have been obtained without any cobalt oxide addition."

From all these opinions it follows that the correct explanation for the action of cobalt oxide upon ground enamels has not yet been given, and that the view expressed by the author of this book ‡ with regard to practical requirements is correct when he

* *Ibid.*, repeated word for word. † *Sprechsaal*, 1908 (No. 36).

‡ Grünwald, *Theory and Practice of Enamelling on Iron and Steel.* C. Griffin & Co., London, 1909.

states that cobalt oxide possesses valuable physical properties which make it specially suitable for the preparation of ground enamels. The property imparted is, that the coefficient of expansion approaches as near as possible to that of the sheet iron. Modern enamelling technology is ever trying to replace dear materials by cheaper ones having the same effect, and has achieved a certain measure of success in the substitution in ground enamels of the much more inexpensive nickel oxide for the cobalt variety. It is indeed possible that cobalt oxide prevents oxidation of the carbon in the sheet iron, since cobalt-free enamels exhibit a silver-like iron surface when chipping takes place, having a colour such as only appears with absolutely pure, unoxidised, carbon-free iron.

As long as no definite investigations have been undertaken, it would be futile to enter into more or less hazardous hypotheses. Every practical enamelling expert knows, however, that a ground enamel free from cobalt and nickel oxides is unobtainable. Each one of us has certainly made countless experiments on the above subject, and often believed one's self near the goal, only to be deceived by tests on the large scale, and so compelled to return to earlier experience.

According to the present position of enamelling technics, only the most urgent advice can be given against the use of ground enamels free from cobalt or nickel oxide. Experiments on the small scale, which are apparently successful, are not sufficient before endangering the whole manufacture. Although nickel oxide * is excluded for white grounds when certainty is required on a large scale, it may replace cobalt oxide, wholly or partly, for many of the cheaper enamels. Many famous enamelling firms, however, celebrated for the excellent quality of their wares, only employ cobalt oxide for their ground enamels.

Owing to the relatively cheap price of cobalt oxide at the present time, the financial advantage by replacement or omission of the cobalt or nickel oxide stands in no ratio to the risk which the good name of the firm undergoes. A brief calculation will make this apparent.

In 100 kg. of fused ground enamel there is at the most 0·6 kg. of cobalt oxide present. One kg. cobalt oxide costs 27 francs (meanwhile the price of cobalt oxide has even sunk to 13 to 14 francs). 600 grammes cobalt oxide accordingly cost 16·20 francs. The 100 kg. ground enamel serve to ground about

* See under *Nickel Oxide*.

1,000 kg. of prepared wares. (On the average it may be assumed that 100 kg. enamelled sheet-iron utensils necessitate 9 to 10 kg. of ground enamel.)

If, instead of the 600 grammes cobalt oxide, there are taken 600 grammes of nickel oxide at only 4 francs per kilo., the economy is 16·20 to 2·40 = 13·80 francs per 1,000 kg. of prepared wares, or 1·38 francs per 100 kg. wares. Such an amount would be important for cheap export wares, but should not be taken into account for wares of quality.

Ground enamels, as a rule, contain 0·5 kg. cobalt oxide per 100 kg. raw enamel, or

0·2	%	cobalt oxide	+ 0·3	%	nickel oxide	+ 0·2	%	pyrolusite.	
0·16	%	„	+ 0·2	%	„	+ 0·15	%	„	
0·08	%	„	+ 0	%	„	+ 1	%	„	*
0·3	%	„	+ 0	%	„	+ 0·7	%	„	
0·16	%	„	+ 0·2	%	„	+ 0·15	%	„	

With these relative data for proved ground enamels, the series of possible combinations is obviously not exhausted. On the average 0·4 to 0·5 per cent. cobalt oxide can be taken for good ground enamels.

Cobalt Oxide in Blue Enamel.—The rôle of cobalt oxide in blue enamel is very simply understood, inasmuch as the property of all cobalt compounds is to dissolve in glasses, enamels, etc., with production of a blue colouration—*i.e.*, with formation of cobalt silicate. The addition of cobalt oxide to the raw enamel usually varies between 1 and 1·6 per cent., although with 1 per cent. a beautiful dark blue enamel is generally obtained.

In many cases, where less depends upon pure blue shades than upon the preparation of a dark bluish-violet enamel, a part of the cobalt oxide may be replaced by pyrolusite—*e.g.*, 0·6 to 0·8 per cent. cobalt oxide + 1·2 per cent. pyrolusite. A small addition of iron oxide (0·1 per cent.) also often intensifies the effect. For special enamels, such as blue enamels for decorations, where an intense pure dark-blue colour is required, the cobalt oxide content may rise to 3 per cent. Important and much underestimated is the fact that, for the complete utilisation of the cobalt oxide added to the raw mixture, it is indispensable to mix this very intimately with the other components. The more attention paid to this point, the more powerful is the effect of the cobalt oxide, while in addition the blue colour appears more

* Less worthy of recommendation.

uniform after the fusion. In order to acquire this intimate mixture with the relatively small amount of cobalt oxide to hand, the following procedure is recommended :—The cobalt oxide (*e.g.*, 1 kg.) to be mixed with 1 portion raw enamel (*e.g.*, 100 kg.) is, first of all, intimately ground (for ten minutes) with a part of the quartz or felspar (*e.g.*, with 10 to 15 kg. felspar) at the dry mill, and this mixture is then added to the main portion. The latter must then be mixed for a longer interval (according to the coarseness of the sample) in the drum—*e.g.*, for 15 to 30 minutes.

For small portions—*i.e.*, up to 100 kg.—hand mixing by means of iron rakes is recommended. For blue enamels of special beauty small portions are preferable.

Recent investigations by Lukas * have demonstrated a not inappreciable wastage of cobalt oxide on heating.

Lukas, from finely-ground cobalt oxide with addition of water and a little glutinous matter, made threads in a rope press, which he dried in warm air and cut into small rods. The surfaces of the rods were rubbed with emery paper, and their length and thickness measured by a screw micrometer. The rods were then heated in an electric platinum resistance furnace, or ultimately at high temperatures in the iridium furnace, and Lukas measured not only the temperature influence, but also the effect of rapid and prolonged heating, upon the decrease. In one series of experiments he subjected the rods at once to the high temperature desired, while in a second series the temperature was allowed to rise gradually (about 100° C. in ten minutes). The following table was compiled, in which the original diameter of the rods (about 1·4 mm.) is made 100 :—

Temperature. °C	Mode of Heating.	
	Rapid.	Prolonged.
700	95·9	97·7
800	90·4	94·7
900	87·4	91·8
1,000	86·3	90·2
1,100	84·0	87·8
1,200	81·6	85·2
1,300	78·9	81·2

* *Zeitschrift für physikalische Chemie.*, vol. lii. (1905), p. 327.

It will be seen that the diminution at 1,000° C. amounts to about 14 per cent.

Cobalt Oxide for the Preparation of Ceramic Pigments and Colours.—Cobalt compounds generally, serve for the preparation of blue pigments, although more rarely copper oxide is used.

We will limit ourselves to giving a few examples :—

For *Sky Blue*,* 14 parts cobaltous carbonate,
20 parts zinc hydroxide,
and 160 parts flux material,

are mixed together and melted. The following serves as a flux :—Quartz 45 parts, red lead 35 parts, potash 18 parts, sand 8 parts; or one lead free, sand 3 parts, chalk 1 part, and calcined borax 3 parts.

Turkey Blue.—50 flux.
0·5 cobalt oxide.
2·5 copper oxide.

Blue.—100 quartz.
50 borax.
200 red lead.
6 cobalt oxide.

Black.—100 quartz.
50 borax.
200 red lead.
1 cobalt oxide.
1 copper oxide.
3 manganese oxide.
2 red iron oxide.

Dark Violet.—90·4 flux.
9 manganese oxide.
9·6 cobalt oxide.

See Chapter XVI. for examples of the percentage composition and practical limits for 100 kg. of raw mixed ground and blue enamels.

* Hermann, *Die Glas-, Porzellan-, und Emailmalerei.*

XII. SODA OR SODIUM CARBONATE,

$Na_2CO_3 . 10H_2O$.

Soda plays an important part in enamel manufacture, and, therefore, merits detailed attention. Artificial soda crystallises in the monoclinic system in the form of sharp rhombic tables with a double row of border faces.

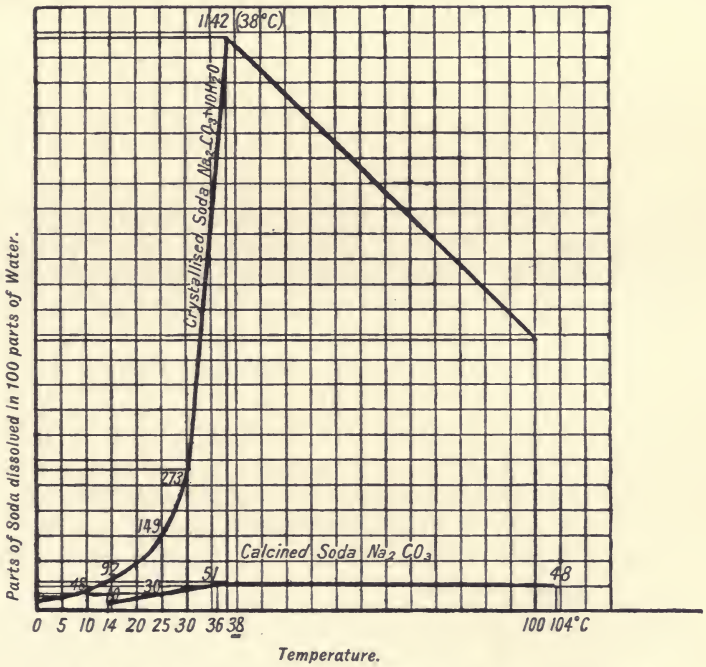

1142 (38°C)
Crystallised Soda $Na_2CO_3 + 10H_2O$
Calcined Soda Na_2CO_3
Parts of Soda dissolved in 100 parts of Water.
0 5 10 14 20 25 30 36 38
100 104°C
Temperature.

Fig. 12.—Solubility Curves of Crystallised and Calcined Soda.

Soda crystallises with 10 molecules of water of crystallisation, and has the formula $Na_2CO_3 . 10H_2O$, corresponding to—

21·67 per cent. Na_2O,
15·36 per cent. CO_2,
62·86 per cent. H_2O.

It melts at 32·5° C. in its crystallisation water, and gives thereby a saturated solution of the hydrate which, on further heating, precipitates a pulverulent hydrate, $Na_2CO_3 . 2H_2O$; the latter loses 1 molecule water in dry air, and, finally, all its water at 100° C. The composition of this anhydrous or calcined soda (which is always used for enamelling purposes) is—

58·50 per cent. Na_2O,
41·50 per cent. CO_2.

Anhydrous soda attracts water from the air without, however, dissolving; it melts at 850° C. with a slight loss of carbon dioxide, and at a very high temperature volatilises. With respect to its solubility in water, 100 parts of water dissolve—

At 0° C., ... 7 parts.
,, 37·5° C., . . . 59·5 parts.
,, 100° C., . . . 45·1 parts of calcined soda.

It will be seen, therefore, that the solubility decreases at higher temperatures, while calcined soda is less soluble than crystallised, as shown by the previous solubility curve (Fig. 12).

Preparation of Soda.—Soda may be obtained (*a*) as natural soda, (*b*) from plant ashes, and (*c*) by chemical methods.

(*a*) In the mineral waters of Carlsbad, Vichy, the Geisir Islands, etc., it generally occurs as a mixture of bi- and sesqui-carbonates. In many districts of Hungary, Asia, and Africa, natural soda effloresces from the ground during the hot season of the year often to thicknesses of 30 to 40 cm. (Tibet). The soda lakes of Arabia, Tibet, and Armenia contain up to 23 per cent. of normal soda. This natural soda is calcined to convert the bicarbonate to carbonate.

In Egypt, natural soda arises from the reduction of sodium sulphate (Na_2SO_4) by fungi and algae to sodium sulphide, this being decomposed by the moist carbonic acid of the air with evolution of sulphuretted hydrogen.

$$Na_2S + CO_2 + 11H_2O = Na_2CO_3 . 10H_2O + H_2S.$$

From the soda lakes close to the Caspian and Black Seas a salt is deposited of formula $Na_2CO_3 . NaHCO_3 . 2H_2O$ ($\frac{3}{4}$ sodium

carbonate), which in Egypt is termed "trona," and in Columbia "uras." Only the deposits of Owen's Lake, Inyo County, California, however, possess great economic significance, and from its waters large quantities of very pure soda may be recovered by simple crystallisation.

(*b*) *Soda from Plant Ashes.*—Before the development of modern chemical processes for manufacturing soda (Leblanc, Solvay, etc.), the major portion was prepared from the ashes of sea and beach plants (*Chenopodium, Salsola, Atriplex, Salicorina,* etc.); these plants abstract sodium salts from the sea, while land plants require potassium salts, and, therefore, potassium carbonate (potash) is contained in their ashes. Beach plants flourish particularly in South France and Spain; (Barilla or Alikante soda, Salicor from Narbonne; Blanquette from Aigues-Mortes; from Tangiers; Varec soda in Bretagne and Normandy; kelp in Great Britain). The Spanish soda reached a high value on account of its high soda content, and for a long time ruled the market.

The recovery of soda from plant ashes is analogous to potash extraction from wood ashes.

The crude soda so obtained is purified by solution in water at 40° C., whereby the carbonate, sulphate, and chloride are dissolved. The pure soda is separated from the latter compounds by heating the solution to boiling, whereby the pure normal sodium carbonate separates out, while the other salts remain behind in solution.

(*c*) *The Chemical Manufacture of Soda by the Leblanc and Solvay* (*ammonia soda*) *Processes.*—At present industrial soda is chiefly obtained by these two processes, and in this respect the Solvay process has attained great importance during the last ten years.

The Leblanc Process.—At the end of the eighteenth century, and at the time of the French Revolution, difficulties occurred in France with reference to soda (from Spain, etc.), by which its export from neighbouring states was rendered impossible by political circumstances. The National Convention accordingly offered a prize for a new chemical method for preparing soda. Nicolas Leblanc solved this problem with brilliant success, and his method underwent further important improvements during the succeeding years. The principle of the Leblanc process is as follows:—Sodium chloride (common salt, NaCl), is converted

into sodium sulphate (Glauber's salt, Na_2SO_4), by heating with sulphuric acid :—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

At the same time, hydrochloric acid is evolved, the process constituting the most useful method for the manufacture of this commercially important acid.

Recently Glauber's salt has been prepared by the action of sodium chloride on magnesium sulphate ($MgSO_4$) at the temperature of winter, and the process is worked at Stassfurt, where large deposits of magnesium sulphate (kieserite) occur :—

$$2NaCl + MgSO_4 = MgCl_2 + Na_2SO_4.$$

The sodium sulphate prepared according to one or the other method is then mixed with excess of coal and limestone or chalk (calcium carbonate, $CaCO_3$), and heated to redness in a reverberatory furnace. The coal used must be of a rich quality, or an anthracite with 15 per cent. ash content at the most. Thereby the sodium sulphate is reduced to sodium sulphide (Na_2S) with liberation of carbon dioxide :—

$$Na_2SO_4 + 2C = Na_2S + 2CO_2.$$

The sodium sulphide then reacts with the limestone or chalk, forming calcium sulphide (CaS) and soda (Na_2CO_3) :—

$$Na_2S + CaCO_3 = CaS + Na_2CO_3.$$

At the same time a part of the calcium carbonate is decomposed at the high temperature attained to calcium oxide (lime, CaO), and carbon dioxide (CO_2), the latter being reduced by the red-hot coal to carbon monoxide :—

$$CaCO_3 = CaO + CO_2.$$
$$CO_2 + C = 2CO.$$

The appearance of the blue carbon monoxide flame, the so-called " candles," denotes the end of the operation.

Recently the soda melt has been carried out in a so-called revolving furnace, using

100 kg. sodium sulphate,
104 kg. calcium carbonate,
53 kg. coal.

Welden recommends a mixture of

100 parts sulphate (Na_2SO_4),
80 parts chalk ($CaCO_3$),
38 parts coal (C).

By the excess of sulphate he aims at preventing the formation of sodium cyanide (NaCN) through the action of carbon on sodium in the presence of nitrogen, which would mean a loss in sodium. The mixture is introduced into the trough *c* of the furnace (Fig. 13), the cover of which is fairly flat, and the flames are drawn over, and so play upon it. The whole is then raked into the trough B, which is then strongly heated (to red heat). Here the real reaction takes place ; the mass foams, yields, and finally becomes liquid, carbon monoxide then being evolved, which burns and dries the mass in C before passing up the chimney. These flames serve at the same time for heating the concentration pans D and E, and so form part of a continuous process.

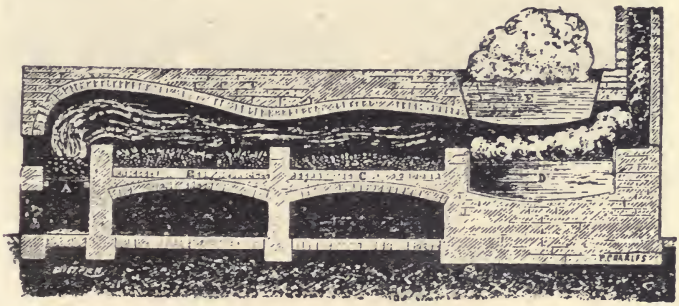


Fig. 13.—Furnace for the Leblanc Soda Process.

The charge is raked from time to time, in order to bring about a uniform melt. The thinly liquid substance is then conveyed to a flat iron apparatus, where it quickly solidifies. The result is now impure crude soda. To avoid hand stirring in the furnace the so-called revolving furnace is at present in vogue, which rotates about a horizontal axis, through which the hot gases are introduced.

This furnace (Fig. 14) consists of a cylinder B, B with horizontal axis, lined inside with fireproof material, and rotated about the axis by a cog-wheel system G, G, F, F between the fire-hearth and the chimney. The flame is drawn into the chimney C, and

entering at A brings the mass to a red heat, leaving the cylinder on the right, while it serves at the same time for heating the evaporating pans containing soda solution (from the later refining process). Inside the furnace are two arms fixed diametrically, which intimately mix the mass during rotation, and so render possible a homogeneous product. The charging takes place at D, and the mass is introduced from the small truck E. When the operation is at an end, the melt is emptied at H.

As we have seen previously, carbon monoxide is formed in the interior of the furnace during the process, and is valuable because of its combustible character, in consequence of which an indirect recovery of the heat expended thereby ensues.

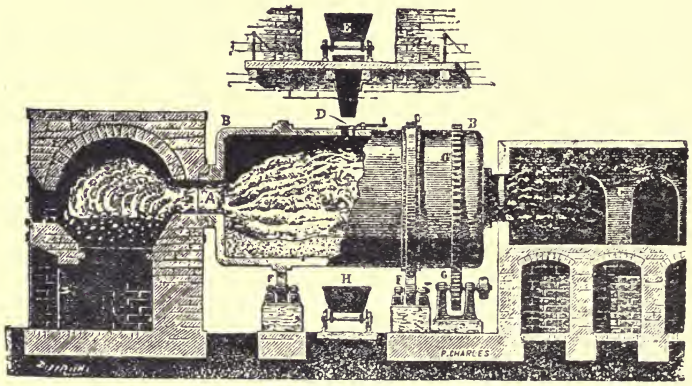


Fig. 14.—Revolving Furnace for the Leblanc Soda Process.

The crude soda now consists of a dirty black mixture (termed black ash) of sodium carbonate, calcium sulphide, calcium carbonate, quicklime, coal, and foreign matters.

This is now systematically extracted by cold water in a specially constructed apparatus, when the soda goes into solution. The residue remaining behind consists essentially of calcium sulphide, calcium carbonate, coal, and foreign matter.

In consequence of its calcium sulphide content, which reacts with water to form sulphuretted hydrogen (H_2S) :—

$$CaS + H_2O = H_2S + CaO,$$

the crude soda has the disagreeable odour of rotten eggs, and contains about 37 to 45 per cent. of pure soda.

The following is the composition of a crude soda :—

Neutral sodium carbonate = soda =	Na_2CO_3, . .	41·0 per cent.
Calcium sulphide,	CaS, . . .	30·0 ,,
Quicklime,	CaO, . . .	10·0 ,,
Calcium carbonate (undecomposed),	$CaCO_3$, . .	5·0 ,,
Common salt,	NaCl, . . .	2·5 ,,
Sodium sulphide,	Na_2S, . . .	1·0 ,,
Sodium and aluminium silicates,	$\left\{ \begin{matrix} Na_2SiO_3 \\ Al_2(SiO_3)_3 \end{matrix} \right\}$.	3·2 ,,
Iron oxide (from the chalk),	Fe_2O_3, . .	2·5 ,,
Unburnt coal,	C, . . .	4·8 ,,

Air and fuel gases (carbon dioxide) are conducted through the crude soda before evaporation, in order to convert any caustic soda which may be present into soda :—

$$CaO + H_2O + Na_2CO_3 = CaCO_3 + 2NaOH.$$
$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

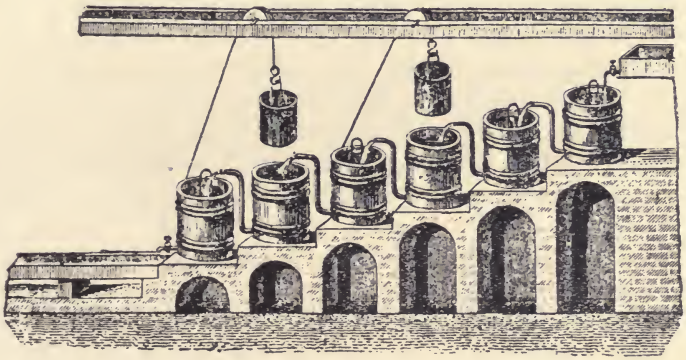


Fig. 15.—Battery of Lixiviation Tanks for the Leblanc Soda Process.

At the same time, the dissolved sulphides are oxidised to sulphates.

The lixiviation of the black ash ensues as follows (Fig. 15) :— The ash is broken into pieces and charged into baskets made of sheet iron, which by suitable gearing are suspended in extraction tanks, the latter being arranged in step-like order.

The uppermost tank is filled with pure water, and the tanks are in communication with each other by means of pipes, which are fixed at the base and dip into the upper part of the tank below. The soda solution flowing from the lowest tank is conveyed to a large clarifying basin. The solution is naturally more

concentrated the longer it has flowed through the tanks, and passes into the basin in this concentrated condition, while the insoluble residue remains behind in the baskets. The soda solution usually possesses a concentration of 28° (Baumé), and is conveyed to the concentration apparatus after all the impurities carried along have settled in the basin. As already noticed, the apparatus is heated by means of the flames drawn along to the chimney. At the beginning the evaporation is rapid, but later the solution has to be concentrated in pans arranged in cascade form. Those evaporation pans are so installed that the concentrated solution is brought near to the flames in the fore part of the furnace, in order that the hottest gases may be applied to the highest concentrates. The soda solution is evaporated until the solvent water has disappeared.

The soda so obtained is a white, strongly alkaline salt, containing about 70 to 80 per cent. of sodium carbonate (Na_2CO_3). The remaining 30 to 20 per cent. consists of caustic soda, common salt, and Glauber's salt.

Rapid evaporation of the soda solution in the boilers D and E at the open fire of the melting furnace affords a soda which is very caustic, owing to the large caustic soda content ; when the consistency reaches 34° Bé., it is further heated in a tank furnace, which already contains crystallised soda, whereby a vigorous decomposition of the carbonate partly begins. The heating is continued with frequent stirring until the mass acquires a paste-like concentration, when it is then allowed to cool. The soda so obtained is crushed into small pieces, and contains from 60 to 70 per cent. pure soda and 15 to 17 per cent. caustic soda, the rest being common salt and sodium sulphate.

The soda meal is now dissolved in hot water until the concentration reaches 33° Bé., when it is allowed to crystallise. The large rhombic soda crystals ($Na_2CO_3 . 10H_2O$) so obtained are allowed to dry, and are then packed in tight casks. If the mother liquor be further concentrated, very little crystalline soda separates.

Pure commercial soda contains 37 per cent. of carbonate (Na_2CO_3), 62 per cent. of water of crystallisation, and only 1 per cent. of common salt and sodium sulphate ($NaCl + Na_2SO_4$).

This small amount of mixed chloride and sulphate of sodium may be removed by dissolving the soda crystals in hot water and allowing the solution to cool rapidly accompanied by stirring.

The perfectly pure soda crystals so obtained are very small in contrast to the commercial article.

The soda crystals are calcined—*i.e.*, dried and heated—for general use, to avoid unnecessary freight charges in consequence of the large water content. This product is the anhydrous or calcined soda, and is naturally richer in alkali (58·50 per cent. Na_2O, 41·50 per cent. CO_2).

It is, therefore, advisable to distinguish between soda crystals with 10 molecules of crystallisation water ($Na_2CO_3 . 10H_2O$), and calcined soda without any such water (Na_2CO_3). The chief by-products and residues of the soda manufacture are hydrochloric acid and calcium sulphide. Hydrochloric acid, in consequence of its cheap production, finds extensive employment as a pickling agent, while from calcium sulphide the sulphur is recovered in the form of sulphuric acid, and again enters into the soda process for the preparation of Glauber's salt from common salt—*i.e.*, it is the most important raw material in soda manufacture.

The chemical reactions in working up the calcium sulphides to sulphuric acid are briefly as follows :—

(1) $$\underset{\text{Calcium sulphide}}{CaS} + \underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide}}{CO_2} = \underset{\text{calcium carbonate}}{CaCO_3} + \underset{\text{sulphuretted hydrogen.}}{H_2S}.$$

(2) $$\underset{\text{Calcium hydrosulphide}}{Ca(SH)_2} + \underset{\text{carbon dioxide}}{CO_2} + \underset{\text{water}}{H_2O} = \underset{\text{calcium carbonate}}{CaCO_3} + \underset{\text{sulphuretted hydrogen.}}{2H_2S}.$$

(3) The sulphuretted hydrogen so obtained is collected in gas holders and burnt :—

$$2H_2S + O_2 = 2H_2O + S_2.$$
$$2H_2S + 3O_2 = 2H_2O + 2SO_2.$$

According to the amount of air for combustion the sulphuretted hydrogen is converted into water and sulphur or sulphur dioxide (sulphurous acid) respectively. Sulphurous acid may readily be converted into sulphuric acid.

The Solvay Ammonia Soda Process.—This process is by far the most important of the modern processes for soda manufacture, and the soda obtained thereby is termed ammonia soda, because ammonia plays an important part in the operation.

The principle of the process is very simple, and depends on the reaction between a saturated solution of sodium chloride

and ammonium bicarbonate [$(NH_4)HCO_3$], whereby ammonium chloride (sal-ammoniac, NH_4Cl), and sodium bicarbonate ($NaHCO_3$) are formed :—

$$NaCl + (NH_4)HCO_3 = NaHCO_3 + NH_4Cl.$$

In 1855, Schloesing and Rolland had already tried with success to produce soda direct from sea salt by the aid of another carbonate—viz., ammonium carbonate—and in 1863 E. and A. Solvay repeated these experiments with such success that in 1873 they founded a soda works at Charleroi in Belgium and at Verangéville-Dombasles in France.

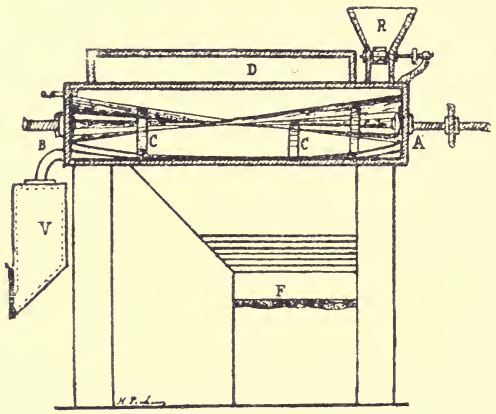


Fig. 16.—Calcination Furnace for the Ammonia-Soda Process.

As already noticed above, the essence of the Solvay process is the reaction between common salt and ammonium bicarbonate to form sal-ammoniac and sodium bicarbonate. A temperature of 30° C., however, must not be exceeded, since below this temperature sodium bicarbonate is insoluble in presence of sal-ammoniac (NH_4Cl). As a rule, ammonium bicarbonate itself is not employed in the Solvay process, but gaseous ammonia and carbon dioxide, which are allowed to act on a solution of common salt.

The carbon dioxide is produced by heating limestone to redness in a special kiln, while the sodium bicarbonate obtained is carefully calcined in a furnace (see Fig. 16), where decomposition takes place into anhydrous soda and carbon dioxide. The latter is again utilised in the process :—

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The calcining furnace consists of a fixed cylinder A B, on whose horizontal axis are fixed three helicoidal blades C, which rotate and cut up the salt mass, forcing it from one end A of the cylinder to the other end B. At the same time the flames from a hearth F beneath the cylinder spread throughout the interior of the furnace.

In the ball-like section at R the sodium bicarbonate is dried before calcination by means of the hot gases. The carbon dioxide has its exit at A, and is collected in a gas holder. If the drying of the bicarbonate before calcination has been well executed, then afterwards a snow-white, powdery, calcined soda is obtained. If the contrary has been the case, then the soda emerges in the form of conglomerated balls.

Some firms employ prepared ammonium bicarbonate in place of gaseous ammonia and carbon dioxide.

The ammonia used in the Solvay process is for the most part recovered from the by-product sal-ammoniac, and returned to the process. The sal-ammoniac, which is in solution, is decomposed by the addition of milk of lime (dissolved lime, $Ca(OH)_2$), forming soluble calcium chloride ($CaCl_2$), and evolving gaseous ammonia :—

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O.$$

The raw materials for the ammonia soda manufacture are accordingly common salt and limestone, which, by the intermediate agency of ammonium salts, are converted into soda and calcium chloride. In place of limestone and lime, magnesite ($MgCO_3$) and magnesia (MgO) may also be employed.

The production of soda by the Leblanc process has been appreciably diminished by this ammonia-soda method, and only in England does the former still retain its original importance.

Finally, the less important process for the production of soda from cryolite ($AlF_3 . 3NaF$) will now be considered. Here powdered cryolite is intimately mixed with lime or chalk and heated to redness, whereby insoluble calcium fluoride (CaF_2) is formed, together with a soluble compound of aluminium and sodium oxides, termed sodium aluminate.

$$2(AlF_3 . 3NaF) + 6CaO = 6CaF_2 + Al_2O_3 . 3Na_2O.$$

The mass is extracted with water, and carbon dioxide which is obtained from a lime kiln is passed through the solution

precipitating hydrated alumina [$Al_2(OH)_6$], and forms sodium carbonate, which remains in solution.

$$Al_2O_3 . 3Na_2O + 3H_2O + 3CO_2 = Al_2(OH)_6 + 3Na_2CO_3.$$

The chief development of the manufacture of soda from cryolite obtains in North America and Denmark, where rich cryolite deposits are found (*e.g.*, at Ivigtut, on the Arksukfjörd, in Greenland, which is Danish territory).

Soda in the Enamel Manufacture.—Soda is only used in the pure calcined condition for enamel preparations. Impurities, such as sulphate or chloride, act injuriously upon the enamel, influencing unfavourably the lustre and resistance to atmospheric agencies. A chemical analysis is therefore made, not only for moisture content, but also for the above-mentioned impurities, as well as for the possible sodium bicarbonate content, since this contains less sodium—*i.e.*, less of the valuable factor concerned.

As already noticed, calcined soda should, for enamelling purposes, be a perfectly pure, fine, friable, brilliant white powder, containing 41·4 per cent. carbon dioxide and 58·6 per cent. Na_2O.

In the enamel preparation soda plays the part of flux, acting exclusively upon the difficultly fusible or infusible silicates present (such as clay, felspar, etc.); it also imparts a bright lustre to the enamel. Ammonia soda is, as a rule, purer than Leblanc soda. The soda content in the raw ground enamel mixture should not usually exceed 3 to 4 per cent. For blue enamels, especially where deep dark-blue shades are in question, many enamelling firms dispense with soda entirely. For lighter blue enamels the soda content amounts to about 3 to 6 per cent. For white enamel, so far as it serves for the first coat, the soda content may vary between 3 and 6 per cent., and for the second or cover white between 3 and 4 per cent.

Restraint in the use of soda is strongly recommended, since the preparation of easily fusible and highly lustrous enamels, by means of larger amounts of soda, is very alluring. All enamels rich in flux, and especially in alkalies, are less durable, easily attacked by organic acids, and even by boiling water in some cases, and readily become dull in consequence of the solubility of the alkali. With coloured enamels, such as blue, red, etc., excess of alkali readily promotes an ugly superficial efflorescence

of alkali salts, which give an unsightly appearance to the wares after storage.

The annual consumption of soda for enamelling purposes by German firms may be estimated, on the basis of Dr. Wuppermann's* data of production, whereby about 90,000,000 kg. of enamelled wares are produced, at least at 750,000 kg. (assuming 28 per cent. of enamel consumption).

These figures do not include those not insignificant amounts of soda, which are annually consumed in the pickling processes of modern enamelling works.

Germany imported and exported in 1908 the following quantities :—

	Import.	Export.
Crude soda, . . .	60,400 kg.	94,300 kg.
Calcined soda, . .	293,300 kg.	257,300 kg.
France, . . .	83,500 kg.	69,504,100 kg.
Austria-Hungary, .	411,300 kg.	1,803,700 kg. (of value 221,000 kr.)

* *Die Industrie emaillierter Blechgeschirre.*

XIII. SALTPETRE.

The nitrates or nitric acid compounds of potassium, sodium, barium, or strontium are also known as potash, soda, barium, or strontium saltpetre or nitre respectively. For enamelling purposes only the potassium and sodium saltpetres are important.

Potassium Saltpetre (KNO_3).—This compound crystallises in the rhombic system, and the crystals cleave in the direction of the rhomboid. They are generally colourless, being transparent to translucent, with a relatively high light refraction, and possess a briny taste. When pure it has the chemical formula KNO_3, possessing 46·58 per cent. K_2O and 53·42 per cent. N_2O_5, whereas crude soda saltpetre (soda nitre) is usually contaminated with much common salt and some sodium sulphate. It is readily soluble in water, deflagrates on red-hot charcoal more vigorously than soda nitre, and melts in the blowpipe flame on platinum foil.

Saltpetre exhibits great solubility in water, which increases with rising temperature, as shown by the following table and diagram (Fig. 17) :—

At	0° C.	100 parts of water	dissolve	12	parts saltpetre.
,,	10° C.	,,	,,	22	,,
,,	20° C.	,,	,,	34	,,
,,	30° C.	,,	,,	48	,,
,,	40° C.	,,	,,	65	,,
,,	50° C.	,,	,,	85	,,
,,	57° C.	,,	,,	100	,,
,,	65° C.	,,	,,	126	,,
,,	80° C.	,,	,,	169	,,
,,	98° C.	,,	,,	238	,,
,,	116° C.	,,	,,	333	,,

This variation of solubility with temperature is utilised for the purification of saltpetre, since it is usually accompanied by other less soluble nitrates.

On heating, potassium saltpetre melts in its water of crystallisation, and at a higher temperature decomposes into nitrogen, oxygen, and potassium oxide, although at a somewhat lower temperature it splits up with evolution of oxygen into potassium nitrite.

$$2KNO_3 = 2KNO_2 + O_2.$$

Owing to this evolution of oxygen the saltpetre acts as an energetic oxidising agent upon its environment, a circumstance which explains many facts when using saltpetre for enamel preparations. By contact with glowing carbon it forms potassium carbonate (potash) with liberation of carbon dioxide and nitrogen.

$$4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 2N_2.$$

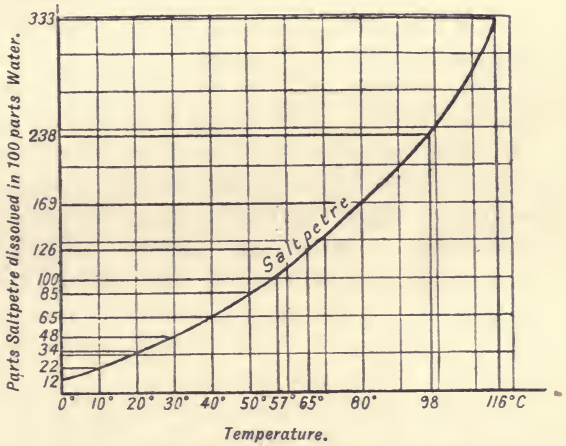


Fig. 17.—Solubility Curve of Saltpetre, KNO_3.

Saltpetre is, therefore, able to oxidise any impurities in the raw materials of organic character to carbon dioxide, and to prevent discolouration of the enamels by the carbon of the organic impurity.

The Saltpetre Manufacture.—Potassium nitre is found in small quantities in the hollows of many limestone mountains (saltpetre caves) in Ceylon, Calabria, Leonhard's Cave at Homburg, Belgrade, etc.; also as an efflorescence (from the ground) in Aragon (Spain), Hungary, and the East Indies; in Hungary, however, it is only found in the immediate neighbourhood of settlements where nitric acid is formed from excrement. Important deposits are worked in Algiers, Chili, and at Tacungo in Quito. Potash nitre

is dimorphous—*i.e.*, it occurs in both the rhombic and rhombohedral systems. The chief production of potash nitre at the present time is by the chemical decomposition of soda or Chili saltpetre, which occurs naturally in huge quantities, by means of potassium chloride (conversion saltpetre).

The Direct Preparation of Natural Saltpetre.—Earlier, potash nitre was exclusively obtained from natural efflorescences on the Nile banks, India, America, South France, etc. To-day the artificial preparation is carried out by the aid of potash-containing minerals, which are soaked with nitrates, or by means of ammonium salts, which are converted by nitrogenous ferments into the corresponding ammonia saltpetre (method of Müntz and Schloesing).

In Ceylon, India, Hungary, Switzerland, France (Longpont), and Sweden, and in certain masonry whose materials contain potassium and which are penetrated by nitrogenous liquids (urine, etc.), potash nitre is to be found.

In Ceylon the excrement of the bat, which is found in large deposits in felspar quarries containing lime and magnesia, furnishes the necessary nitrogenous matter for nitrification. The saltpetre rocks of Ceylon usually contain only 3 per cent. potash nitre, 1 per cent. nitre [$Mg(NO_3)_2$], 27 per cent. pure chalk ($CaCO_3$), and 61 per cent. felspar, mica, and quartz. According to Berzelius, the nitrogen of the air and of the organic substances is oxidised by contact with the porous rocks to nitric acid. The saltpetre then separates on the outer surface as an efflorescence.

These rocks are afterwards broken up into fragments, pulverised, and mixed with wood ashes (containing K_2CO_3), to enrich the potassium content. The potash nitre formed is extracted with hot water, whereby the magnesium nitrate present is converted into the potassium salt, leaving magnesia behind. The mud is allowed to settle, a part of the water evaporated by aeration, and the clear solution withdrawn to be concentrated direct in heated pans.

At Patna, in Bengal, the potash nitre is found in the form of a crust-like efflorescence during the dry season. This crust has the following composition, according to Davy :—

8 per cent. potash nitre.	35 per cent. pure chalk.
4 per cent. lime nitre.	12 per cent. water and organic matter.
0·2 per cent. common salt.	
0·8 per cent. earthy sulphates.	40 per cent. insoluble matter.

The saltpetre is here obtained by extraction, without, however, the employment of wood ash.

In the neighbourhood of Theiss, in Hungary, are earths which contain lime and are rich in clay together with porous black sand. The organic substances containing nitrogen, from the neighbouring farms, sink into the ground, and are covered from time to time with wood ashes. The nitrification is very vigorous. The efflorescence is collected and the nitre extracted as above. On an average a saltpetre harvest is garnered six times a year from these nitre plantations, 1 hectare furnishing about 400 kg. of saltpetre.

In Switzerland the ground of cattle stalls is washed every seven years, lime and wood ashes being added to the washings, which, after settling, are concentrated and the saltpetre crystallised out. This saltpetre contains—

90 per cent. KNO_3,
3 per cent. $Ca(NO_3)_2$,
7 per cent. water and insoluble matter.

At Longpont (France) saltpetre is manufactured in quarries. The ground is covered with alternate layers of stable dung and earth, 10 cm. thick, and the whole saturated with liquid manure. After two years the heap is turned over, and after a further two years extracted with water.

The urine from twenty-five head of cattle furnishes in this way 600 kg. of impure saltpetre. The latter is recovered in Sweden by a similar method.

Within recent years the nitrogenous ferment has been discovered by Müntz and Schloesing, so that saltpetre may now be made artificially. The conditions for developing the ferment are nitrogen-containing salts (sal-ammoniac, etc.), together with potash, lime, and magnesia for fixing the nitric acid when formed; sufficient moisture and air access; temperature between 15° and 20° C., and the presence of a nitrogenous ferment which is artificially cultivated. A humus-rich ground is most suitable for stable dung, street refuse, and waste of an organic character. Masses of such material are built up into pyramidal heaps and saturated with urine, whereby a part of the nitrogen is lost as ammonia. After an interval the saltpetre appears as a superficial efflorescence, and is recovered pure in the usual way.

The nitrification is appreciably promoted by addition of animal blood, decaying foliage, and stable dung. A solution of

ammonium sulphate ($7\frac{1}{2}$ grammes per litre) is poured over the mass, and a yield up to 5,000,000 kg. of saltpetre per hectare per annum is so obtained.

This kind of saltpetre production has great importance for the future. The crude saltpetre is extracted with water, and the solution evaporated, the product obtained being purified by recrystallisation. The extract is, however, first filtered over wood ashes for the purpose of converting the lime and magnesia nitrates into the potassium salt. On account of the high price of ashes rich in K_2O and K_2SO_4, the extraction is often carried out with milk of lime, whereby the magnesia is precipitated and calcium salts are formed, the calcium being removed as calcium sulphate (gypsum, $CaSO_4$), by addition of sodium sulphate to the solution.

The solution remaining now contains potassium and sodium salts, and by addition of potassium chloride (from Stassfurt carnallite, KCl), followed by evaporation, the sodium nitrate is converted into potash nitre.

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

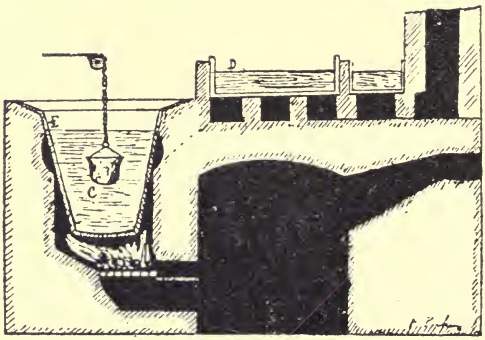


Fig. 18.—Apparatus for Production of Potash Nitre.

The excess of potassium chloride crystallises with the common salt formed even from the hot solution, while the saltpetre remains in solution, and is only obtained crystalline by further evaporation.

The chief method for producing potash nitre, however, is by conversion of the naturally occurring soda or Chili saltpetre with potassium chloride (carnallite) or potash (K_2CO_3).

$$(1) \quad 2NaNO_3 + K_2CO_3 = 2KNO_3 + Na_2CO_3.$$
$$(2) \quad NaNO_3 + KCl = KNO_3 + NaCl.$$

According to Gentele, two separate boiling solutions of pure potash and purified Chili saltpetre are prepared and sufficiently concentrated, so that on mixing small crystals of soda separate. At the same time, any calcium and magnesium carbonates present are precipitated. A gelatinous solution is then added, which coagulates the organic impurities, and carries them down with it to the bottom. The pure fluid is decanted, evaporated, and crystallised.

Since potassium chloride (carnallite) is cheaply produced from the Stassfurt Abraum salts, the conversion of the Chili saltpetre is preferably performed by means of carnallite, because the common salt hereby formed is less soluble than the soda from process 1.

According to Anthon, the soda nitre is dissolved in excess of hot water to which pulverised carnallite is added, and immediately dissolves. By double decomposition, according to equation 2, the major part of the common salt separates out as it forms (since common salt is sparingly soluble in water in presence of potassium chloride and nitrate), and may be removed by a ladle. The solution is concentrated to 42° Bé. with further separation of common salt, and after standing, the clear solution is conveyed to crystallisation vessels, where the saltpetre separates out almost pure (at the most with 1 per cent. impurity of common salt); these crystals are allowed to drain twelve hours for any residual dissolved salt to run away.

The last traces (0·25 per cent.) are removed by refining.

The crude saltpetre obtained after evaporation is still contaminated by 6 to 20 per cent. of other substances, such as chlorides, carbonates, and organic compounds, which render the saltpetre hygroscopic, and so make it unsuitable for many industrial purposes on account of its bad grinding qualities. To remove these impurities Lavoisier and Baumé's process is employed, which consists in first washing the crude saltpetre with a saturated aqueous solution of pure saltpetre, since this can dissolve no more saltpetre, but only foreign salts. The saltpetre is then dissolved in a copper tank (260 cm. diameter and 170 cm. deep). The bottom of this tank should stand at least 50 cm. from the fire-plate. The exact amount of water necessary for solution of the saltpetre is then introduced into the tank (about 12 kg. water per 3,000 kg. crude saltpetre). If, for example, the saltpetre contains 20 per cent. of im-

purities (6 per cent. KCl and 14 per cent. NaCl), then there results—

180 kg. KCl,
420 kg. NaCl,
2,400 kg. pure nitre (KNO_3).

The 1,200 kg. water are able to dissolve at 100° C. :—2,904 kg. KNO_3, 342 kg. KCl, and only 162 kg. NaCl.

This amount of water is, therefore, able to dissolve the whole of the saltpetre and the potassium chloride, while 420 — 162 = 258 kg. NaCl remain insoluble ; in this way a considerable part of the common salt is removed. During the boiling and removal of the separated NaCl, a further 400 kg. water and 1 kg. glue are added (since as mentioned earlier the coagulating albumen carries down the organic impurities to the bottom), the coagulated mass scooped out, the clear solution allowed to stand, and then poured into broad, copper, crystallisation tanks, where it is allowed to cool slowly for six to eight hours. The crystal formation is fairly sluggish. The crystals are collected into heaps, allowed to drain, and the upper dirty layers of the heaps again washed in tanks.

About 600 kg. of mother liquor remains behind, which at 15° C. is able to dissolve a further 174 kg. KNO_3, 159 kg. NaCl, and 198 kg. KCl, and, therefore, is returned to the process. The last traces of common salt are removed by washing with a solution of pure saltpetre in double-bottomed vats.

From 3,000 kg. of crude saltpetre, about 1,800 kg. of refined saltpetre are obtained with quite a small common salt content.

Chili Saltpetre or Soda Nitre.—Over 200,000 tons of Chili saltpetre are annually consumed in Europe, of which the greater part serves for the preparation of potassium nitrate for gunpowder purposes. From the above amount 235,000 tons of KNO_3 are obtained, the market price being about 26 francs per kilo.

Soda nitre, on account of its cheapness (half that of potash nitre), is employed in large quantities in the enamel industry, seldom potash nitre.

It crystallises in the rhombic system, easily cleaves parallel to a face, possesses a briny taste, and when pure contains 36·49 per cent. Na_2O and 63·54 per cent. N_2O_5. It is easily soluble in water, melts before the blowpipe upon platinum foil, colouring the flame yellow. It is found stratified in clay and sand deposits, spread over a large rainless region of about 40 km. in extent at

Iquique and Tarapaca, in Chili, also at Arané in Bolivia. The small crystals of Chili saltpetre contain some included sodium sulphate, chloride, and iodide (NaI). Soda nitre is very hygroscopic in moist air, a property which increases with the impurity content.

A remarkable fact is that of the greater solubility of soda nitre in the cold than the potash variety; the solubility of both salts at 72° C. is the same, while above this temperature potash nitre is appreciably the more soluble compound.

The solubility changes with rising temperature are as follows :—

At	0° C.	100 parts of water dissolve	71	parts of soda nitre.
,,	10° C.	,, ,,	79	,, ,,
,,	20° C.	,, ,,	88	,, ,,
,,	30° C.	,, ,,	98	,, ,,
,,	40° C.	,, ,,	109	,, ,,
,,	50° C.	,, ,,	120	,, ,,
,,	60° C.	,, ,,	131	,, ,,
,,	70° C.	,, ,,	141	,, ,,
,,	80° C.	,, ,,	154	,, ,,
,,	90° C.	,, ,,	166	,, ,,
,,	119·4° C. (boiling point)	,,	214	,, ,,

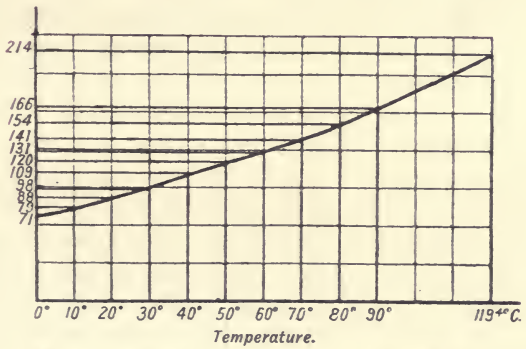


Fig. 19.—Solubility Curve for Soda Nitre, $NaNo_3$.

The aqueous solution of soda nitre forms at 0° C. a hydrate $NaNO_3 . 16H_2O$, but remains liquid down to — 15° C., and only crystallises from the solution at this temperature (*Ditte*). For gunpowder manufacture it is useless on account of its great affinity for water.

The most important deposits are found at Tarapaca in Peru, in the neighbourhood of the western section of the Andes chain,

at a height of 1,000 m. The Chili deposits (*Calicheras*) are less extensive. Crude saltpetre (*Caliche*) is found in irregular heaps over whole land areas, and, as a rule, these are covered by layers of sand and clay (*costra*).

Often two heaps of caliche are deposited one above the other, and in such a case the upper is richer in soda nitre and the lower in common salt. In every case, however, the substratum is formed of common salt. The heaps contain amounts of soda nitre, varying from 20 to 40 per cent., and the recovery is easy or difficult according to the common salt content.

Nöller explains the formation of the saltpetre from sea algae, since the present locality was submerged in earlier times. By slow oxidation the nitrogen-containing algae in combination with the sodium of the sea salt evolved the Chili saltpetre. Other authorities trace the existence of this soda nitre to the decomposed guano (*i.e.*, the excrement) of sea birds, this being extremely valuable as dung, in consequence of its richness in nitrogen.

At distances of 15 m., pits are dug of $\frac{1}{2}$ m. diameter, and filled with a mixture of pure soda nitre, sulphur, and powdered charcoal; the latter is ignited, whereby the whole mass is thrown up without explosion and disintegrated into large fragments, which are further pulverised, and the lumps of clay and sea salt sorted out.

The extraction of the soda nitre next follows, and is based on the fact that its solubility rapidly changes with rising temperature. The presence of sodium chloride lowers the solubility of the saltpetre, so that, for example, 100 grammes water + 25 grammes sodium chloride are now only able to dissolve 53 grammes instead of 88 grammes of saltpetre. The saturated solution of saltpetre boils at 122° C. By concentrating this solution 95 per cent. of the soda nitre is obtained, while a part of the common salt remains behind with the earthy components and sodium iodide (NaI).

The solution is evaporated down in iron pans by direct firing (*Paradas*).

The vessel is filled with a fairly concentrated solution, raised to the boil, and crude caliche added in small lumps, the scum formed together with the insoluble constituents of the salt being ladled off. When sufficiently concentrated, the clear solution is removed and allowed to crystallise in wooden vats (2 m. × 1·5 m. × 0·2 m.) for twenty-four hours. By this means 40 per

cent. crystals and 60 per cent. mother liquor are obtained. The latter serves for the solution of fresh charges, and becomes gradually richer in iodides and iodates. Iodine is then cheaply prepared from this solution.

The crystallised soda nitre of commerce has generally a dirty brownish colour, and is always moist on account of its calcium and magnesium chloride content. It crystallises in rhombohedra whose form closely approximate to the cube. Commercial soda nitre generally contains 94 to 99 per cent. $NaNO_3$ and 2 to 0·4 per cent. NaCl, with traces of calcium nitrate, $Ca(NO_3)_2$, potassium sulphate, K_2SO_4, and a little water.

The saltpetre is transported in sacks, which become impregnated with it, and therefore difficult to burn. By washing these sacks, up to $\frac{3}{4}$ kg. of soda nitre per sack can be recovered.*

Saltpetre Production from Atmospheric Nitrogen.—This process, which is full of promise for the future, has attained special importance in countries possessing cheap electrical energy, whereby the oxides of nitrogen are first formed and their union with lime brought about (for manure purposes). The lime saltpetre may, however, be converted into the potash variety.

This fact alone—viz., that artificial saltpetre can be used for manures in place of the natural Chili compound—is destined in a short time to force down the price of the latter.

The most important installation for the production of artificial saltpetre (Norwegian saltpetre) is found at Notodden in Norway, and in 1909 about 16,000 tons were prepared in this way. The necessary 40,000 horse-power was furnished by the Svälgfoss Waterfall, which has a drop of 46·5 metres. A similar installation at the Rjukan Waterfall, in the upper part of Telemarken, has made such rapid progress that in 1911 the total annual production of saltpetre in Norway reached 40,000 tons, with an expenditure of 125,000 H.P.

The saltpetre production at Notodden depends on the oxidation of atmospheric nitrogen by the rapid passage of this through chambers strongly heated by means of the electric arc.

In 1785 Priestley and Cavendish observed the formation of nitric acid when electric sparks are passed through moist air. Also, if the air be heated to a very high temperature, a part of the nitrogen combines with the oxygen (air consists of about 79 parts nitrogen and 21 parts oxygen).

* In 1910 the exports of Chili saltpetre amounted to 2,335,545 tons.

By means of the recent physico-chemical investigations of Nernst, Van't Hoff, Jellinek, etc., the conditions for combination can be obtained with precision both from a technological as well as a purely scientific standpoint. The necessary temperature for the process must exceed 2,300° C., and the only practical source available for the production of temperatures above 3,500° C. is the electric arc.

At Notodden, in Norway, the following method has proved successful :—By the aid of the electric arc a special furnace is heated to a high temperature and 25 cubic metres of air are passed through per minute. The furnace has, externally, the

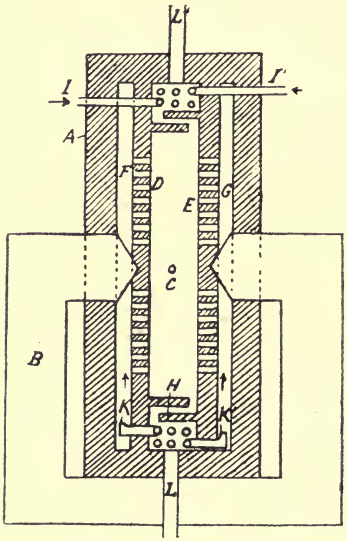


Fig. 20.—Electric Arc Furnace for Fixation of Atmospheric Nitrogen.

appearance of a shallow box, while Fig. 20 (a vertical section) gives the latest construction of the furnace interior (D. R. P., 170,585, Kl. 12*b*). A is the furnace wall and B an electro-magnet, which causes the arc of the alternating current to be spread out into a large shallow disc (shown in Fig. 20 as a small circle C).

The air entering through I and I′ is previously warmed in a tube which circulates the furnace, then passes by means of K and K′ into the chambers F and G, from which it proceeds to the apertures D and E into the central chamber containing the

arc disc, finally having its exit at H and L. Every furnace requires 500 kilowatts. The air from the furnace charged with about 2 per cent. nitric oxide (NO) is conducted up an absorption tower packed with granite slabs, where it meets a descending stream of water, which is repeatedly pumped to the top of the tower, until finally a 50 per cent. content of nitric acid is obtained. Since the water has even yet not absorbed all the nitric oxide from the air, the latter is again passed into absorption towers charged with milk of lime, and through chambers containing solid lime. The total yield is finally worked up and exported as calcium nitrate (lime saltpetre). Naturally the nitric acid so formed can easily be fixed with an alkali, and, therefore, potash or soda nitre can be cheaply produced in a short time. The theoretical treatment from the physico-chemical standpoint, as given by Nernst, is as follows :—Taking the reaction equation,

$$N_2 + O_2 \rightleftarrows 2NO,$$

i.e., 1 vol. nitrogen + 1 vol. oxygen = 2 vols. nitric oxide—we have, therefore, to deal with a reversible and, in consequence, an incomplete or balanced action.

The volume of the gaseous mixture undergoes no change, and accordingly external pressure exerts no influence on the equilibrium.

Since heat is required (endothermic reaction) for the union of nitrogen and oxygen, the formation of the nitric oxide (NO) will be accelerated by temperature increase.

The influence of the mass of the different components of the reaction upon the nature of the equilibrium is determined from the mass action law as follows :—

$$\frac{C_{N_2} C_{O_2}}{(C_{NO})^2} = K,$$ where C_{N_2}, C_{O_2}, C_{NO} represent the respective masses.

Now, the equilibrium constant K changes with the temperature according to the known equation :—

$$\frac{d \log_e K}{d T} = -\frac{\varphi}{2 T^2},$$

where φ is the change of energy in the system, and T the absolute temperature.

Integrating this under the assumption that φ is independent

of the temperature (as it apparently is for all practical purposes in the case now considered), we have for any two temperatures T_0 and T_1 the equation—

$$\log_e K_1 - \log_e K_0 = \frac{\varphi}{2}\left(\frac{1}{T_1} - \frac{1}{T_0}\right).$$

Thus, if we know the equilibrium constant K_0, for temperature T_0, and also the energy change in the system, we can calculate from this last equation what the equilibrium constant will be for any other temperature T_1. The energy change in the system can be determined by finding the equilibrium constant for two temperatures, and then substituting in the above equation. In this way, from a couple of measurements at different temperatures, we shall be in a position to foretell the equilibrium constant of the reactions for any temperature.

The agreement between theory and experiment is quite close, as the following figures * show :—

Temperature.	Percentage NO observed.	Percentage NO calculated.
1,811° C., . . .	0·37 . .	0·35
1,877° C., . . .	0·42 . .	0·43
2,033° C., . . .	0·64 . .	0·67
2,195° C., . . .	0·97 . .	0·98
2,580° C., . . .	2·05 . .	2·02
2,675° C., . . .	2·23 . .	2·35

The thermo-chemical equation runs :—

$$N_2 + O_2 = 2NO - 43{,}200 \text{ calories},$$

i.e., by the union of 28 grammes N with 32 grammes O to form 2×30 grammes NO, 43,200 grammes calories are consumed.

Alfred Hartwig † has contributed a short report on the present position of the Chili saltpetre industry, from which the following abstract is taken :—

On March 3rd, 1908, the Chili Saltpetre Trust went bankrupt, and energetic efforts were made for its reconstruction.

In the year 1908 the	production	amounted to	4,284,726	tons.
,, ,,	consumption	,,	3,992,347	,,
,, ,,	export	,,	4,457,610	,,

* Nernst, *Application of Thermodynamics to Chemistry*, p. 35.

† *Chemiker Zeitung*, No. 13, 1909, p. 1162.

In the year 1908 there existed 118 saltpetre firms (termed Officinas), which number recently decreased owing to the prevailing crisis, so that at present the position of the Chili saltpetre must be regarded as unsound. The export exceeds the consumption, and the latter is distributed among the following countries, as follows :—

Country.	1904.	1905.	1906.	1907.	1908.
Europe, . .	25,589,340	27,418,760	28,552,200	28,643,970	31,673,070
North America (East Coast),	5,512,732	6,131,340	7,425,090	7,162,200	6,337,880
North America (West Coast),	863,023	864,214	724,761	948,211	758,618
Other countries, .	762,481	1,126,968	878,043	1,009,613	1,138,411
Chili (for its own consumption),	31,051	26,945	30,800	33,417	15,510
*Total (quintales),	32,758,627	35,568,227	37,610,894	37,797,481	39,923,489

The consumption of the individual European States has undergone the following interesting fluctuations during two recent years :—

Country.	1907.	1908.	Decrease in Consumption.	Increase.
Germany, . . .	12,555,700	14,134,420	..	1,578,720
France, . . .	5,202,370	6,189,300	..	986,930
Belgium, . . .	3,785,800	4,719,370	..	933,570
Holland, . . .	3,129,610	2,795,190	334,420	..
England, . . .	1,887,150	1,767,780	119,370	..
Italy, ...	964,620	1,035,230	..	70,610
Scotland, . . .	666,310	640,290	17,020	..
Austria, . . .	140,760	175,260	..	34,500
Spain, . . .	133,860	159,850	..	25,990
Sweden, . . .	123,510	47,380	76,130	..
Denmark, . . .	54,280	..	54,280	..
*Total (quintales), .	28,643,970	31,673,070	601,220	3,630,320

The influence which the manufacture of artificial saltpetre has had on the market is shown by the fact that Denmark has made no purchase from Chili since 1907, while Sweden will speedily keep her company.

* To convert to tons (approx.), divide by 10.

The price also of saltpetre fell from 10s. 2½d. in 1907 to 8s. 9d. in 1908.

Regarding the future of the saltpetre industry, the securities offered by the Chilian Government must be received with caution, since hitherto the product has only been regarded by them for revenue purposes, and, in addition, there are political troubles to take into consideration.

According to the latest reports of the trade journals, the annual consumption for France and Belgium is estimated at 300,000 tons and 217,000 tons respectively.

The average price for soda nitre was 23 to 25 francs per 100 kg., and for potassium saltpetre 46·50 francs for pure 100 per cent. product, and 26·50 francs for 65 to 80 per cent. material per 100 kg.

The Rôle of Saltpetre in Enamel.—The consumption of saltpetre in enamel manufacture is not inconsiderable, and, according to the author's estimate, attains over 600,000 kg. annually in the German enamelling works, allowing for an average content of only 2 per cent. saltpetre in fused enamel. The added saltpetre not only functions as a flux in the enamel, in consequence of its alkali content, but also for the decolourisation of an impure enamel melt, on account of the ease with which it gives off oxygen at high temperatures. Organic substances, especially carbon, which is often present after fusing the enamel, either from accidental impurities or from the fuel gases, would readily tint the enamel a yellowish-white.

The oxygen of saltpetre oxidises the carbon to its monoxide and dioxide. On account of this oxidising property it will be necessary, in such cases where the preparation of coloured enamels is in question, to reduce the saltpetre content of the mixture either entirely or to the irreducible minimum. The colouring of white enamels by copper oxide may be mentioned at this point, the latter being added at the melting. According as the enamel contains saltpetre or not in addition to soda, it is coloured greenish-blue to Turkey-blue, or even light-blue. As a rule, 2 to 4 per cent. saltpetre is added to 100 kg. raw mixture of a ground enamel, 1 to 2 per cent. for white, and 0 to 3 per cent. for blue enamels.

When it is a question of producing a proper dark-blue enamel, no saltpetre must be added, while the converse addition of an opaque cobalt blue is sometimes made; in which case there are

added to the mixtures, besides cobalt oxide, some tin oxide or white waste, and 2 per cent. or often 3 per cent. of saltpetre. The saltpetre in time becomes hard in the sacks, and has then to be pulverised again ; it is, therefore, an advantage to store it in well-closed chests lined with sheet zinc, so that before admixture with the enamel it is dry enough for grinding purposes, whereby as intimate an enamel mixture as possible will be obtained. As a general rule, only quite pure potassium saltpetre is to be recommended. The low price of purified soda nitre, however, causes preference to be given to this when manufacturing on a large scale. In this case an analysis for the chloride, sulphate, and insoluble matter contents is to be recommended before use.

The more expensive potassium saltpetre may safely be supplanted by the cheaper soda nitre for enamel manufacture (in molecular proportions, of course).

XIV. POTASH (K_2CO_3).

Potash, termed potassium carbonate, is a component of the ashes of land plants. Since 1,000 parts of wood furnish 3·5 to 28 parts of ash, containing 0·45 to 4 parts of potassium carbonate, only well-wooded countries can produce this salt from wood ashes on the large scale. The wood ash is extracted with water, the clear solution evaporated until it solidifies on cooling, and the solid mass finally calcined in the furnace for removal of water and colour. The crude potash so obtained undergoes a second similar purification, and furnishes purified potash or pearl ash.

Analyses of Some Wood Ashes.

Component.	Vosges.	Tuscany.	America.	Russia.	French Pearl Ash.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Potash, K_2CO_3, . . .	38·60	74·10	68·00	69·70	71·40
Potassium sulphate, K_2SO_4, .	38·90	13·50	15·30	14·10	14·30
Potassium chloride, KCl, . .	9·10	1·00	8·20	2·10	3·60
Soda, Na_2CO_3, ...	4·20	3·00	5·90	3·10	2·30
Phosphoric acid, silica, lime, etc.,	1·20	0·50	..	1·00	3·30
Water, ...	5·30	7·20	..	8·80	4·60
Insoluble matter, . . .	2·70	0·70	2·60	1·20	0·50

In countries which cultivate the beetroot, such as Belgium, Germany, France, and Austria-Hungary, considerable amounts of potassium carbonate are recovered from the ash. Beetroot extracts from the soil large quantities of potassium salts, which must be returned to it by potash manures (Stassfurt Abraum salts) if continuous efficient conditions are to be maintained. The alkali salts of the beetroot pass into the sap, and after the main portion of the sugar has been removed, they remain in the so-called molasses. The latter are allowed to ferment, after which they are distilled and finally evaporated, the residue being subjected to dry distillation, whereby alcohol, ammonia,

trimethylamine, and other valuable substances are obtained, together with a charred residue rich in potassium carbonate, which is extracted with water and worked up in the usual way. The molasses from beetroot contain 48 to 50 per cent. sugar, 30 to 36 per cent. salts and organic substances, and 15 to 20 per cent. water.

At present the molasses (the syrup) are treated with water and a mineral acid, in order to convert the saccharose—viz., the sugar ($C_{11}H_{22}O_{12}$) into the fermentable monoses, glucose (grape sugar), and lævulose (fruit-sugar), both of which possess

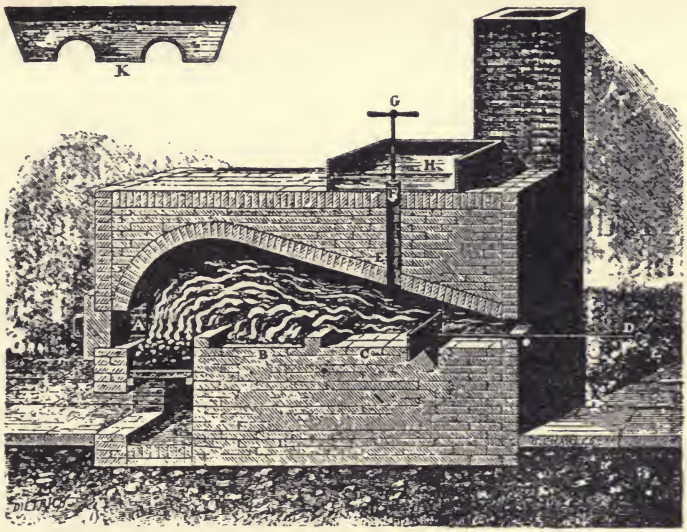


Fig. 21.—Apparatus for Potash Recovery.

the formula $C_6H_{12}O_6$. (This is the so-called inversion of cane sugar.) Under the influence of ferments these monoses are transformed into ethyl alcohol (commonly called "alcohol") and carbon dioxide.

$$C_6H_{12}O_6 + \text{ferment} = 2C_2H_6O + 2CO_2.$$

The alcohol is fractionated in a column apparatus, and there remains behind a mass termed "syrup," whose composition has already been discussed. In order to recover the potassium carbonate from the syrup, the free acid therein is neutralised with chalk, evaporated in the pan K (Fig. 21) to 25° Bé, and the whole

poured into H, from which it passes by the channel E (closed by the stopcock F G) to C, being finally converted into ash in B. The heating must not go so far that the carbon dioxide of the potash is reduced by the organic substance, or the sulphate converted into sulphide (Dubranfant, 1895). To-day, instead of making it into ash only, it is the practice to evaporate the fluid to complete dryness, and afterwards to calcine the residue in a special furnace.

At Courrières 250 hectolitres of alcohol are daily obtained from 90,000 kg. molasses, together with 100 kg. methyl alcohol (CH_4O), 1,600 kg. ammonium sulphate, $(NH_4)_2SO_4$, 1,800 kg. mother liquor containing trimethyl-ammonium chloride, and, as a calcination residue, a black-grey crude potash having 33 per cent. of K_2CO_3.

Considerable quantities of potash are also recovered from the wool-scouring process, since the raw sheep fleece contains about 60 per cent. perspiration and dirty matter, which includes soluble calcium salts of organic acids.

The major part of the potash in Germany, however, is obtained from the Stassfurt deposits (potassium chloride).

(1) By Leblanc's method (see *Soda Manufacture*), which was first employed for potash by H. Grüneberg in 1861.

(2) By C. R. Engel's process at Montpellier and Precht, in which the potassium chloride solution is mixed with magnesium carbonate and carbon dioxide passed through until saturation has taken place, when a double salt of magnesium carbonate with acid potassium carbonate is precipitated, while magnesium chloride passes into solution.

$$3MgCO_3 + 2KCl + CO_2 + 9H_2O = 2(MgCO_3 . KHCO_3 . 4H_2O) + MgCl_2.$$

The double salt is freed from adhering liquor by washing with a solution of magnesium bicarbonate, and then decomposed at 140° C. by water under pressure. Hereby heavy basic magnesium carbonate separates, carbon dioxide being evolved; the solution of pure potash is then evaporated, and the residue calcined. By this process a potassium carbonate free from sodium salts is obtained, since sodium chloride does not react with magnesium carbonate.

Potash may also be obtained by heating felspar to redness in a revolving furnace (see *Soda*) with a mixture of chalk and

fluorspar. In this case a potassium-calcium double silicate is formed, which, when treated with hot water, only parts with its soluble potassium component. The clear solution is drawn off and carbon dioxide passed through it, when the silica is precipitated and a solution of potash obtained. The latter is converted by filtration and evaporation into the pure solid.

The following are some typical analyses of commercial potash :—

	From Wool.	From Molasses.	
		Crude.	Refined.
	Per cent.	Per cent.	Per cent.
Potash, K_2CO_3,	90·5	35	95·2
Potassium sulphate, K_2SO_4,	0·3	5	0·7
Potassium chloride, KCl,	2·1	17	1·7
Soda, Na_2CO_3,	4·3	16	2·1
Phosphoric acid, silica, lime,	2·0	none	0·3
Water, H_2O,	0·8	9	none
Insoluble matter,	none	18	none

Chemically-pure potash is obtained by calcination of potassium bitartrate (Weinstein, Argol), $C_4H_5KO_6$, which separates out in wine casks.

$$2(C_4H_5KO_6) + \text{heat} = K_2CO_3 + 5H_2O + 2CO_2 + 5C.$$

After extraction with water the carbon remains behind as residue, and is thus removed. The clear solution is then concentrated and crystallised.

Potassium carbonate comes on the market as a white granular powder, which is deliquescent (hygroscopic) in the air, melts at about 890° C., and volatilises at a red heat. It crystallises from a concentrated aqueous solution with $1\frac{1}{2}$ molecules of water of crystallisation in monoclinic prisms. At 100° C. it loses only half a molecule of water. The solution tastes caustic and reacts alkaline (red litmus paper is coloured blue). It readily absorbs carbon dioxide from the air with formation of the acid salt or potassium bicarbonate ($KHCO_3$).

$$K_2CO_3 + H_2O + CO_2 = 2KHCO_3.$$

In 1908 Austria-Hungary imported 168,700 kg. of potash, valued at about 61,000 kronen, and, on the other hand, exported

4,296,100 kg. of value 1,324,000 kronen, of which 3,592,600 kg. contained up to 85 per cent K_2CO_3. In the same period Germany imported 1,773,100 kg. of ash from sheep washings (suint), and exported 3,062,200 kg.; this country also imported 1,030,600 kg. of charred sugar residues and exported 2,572,700 kg. The chief quantity of suint came from Austria-Hungary (1,325,100 kg.), and the chief export of German produce went to England (2,500,000 kg.), Sweden (934,000 kg.), United States (596,700 kg.). Of the charred sugar residues 595,500 kg. came from Italy to Germany, and 2,565,100 kg. went to Austria-Hungary.

Potash and the Enamel Industry.—Potash has been used from earliest times for the preparation of glass, and at the present time finds employment in large amounts for making Bohemian crystal glass and other difficultly fusible glasses, being used either alone or with soda. It is a noteworthy fact that double compounds of potassium and sodium are more readily fusible than single compounds of either. When purchasing potash, not only must the moisture content be estimated, but also the total amount of potassium carbonate, since such impurities as iron oxide and alkaline chlorides may occur, these being injurious, inasmuch as they form no compound with the enamel, and may promote blister formation. The total content of the relatively cheaper sodium salts such as soda must also be determined, especially in the case of potash prepared from beet residues, which may frequently contain very considerable quantities of sodium salts.

Potash renders the enamel softer than the chemically analogous soda, while, in general, potassium salts cause the enamel to be more readily fusible than sodium salts. In consequence, therefore, although the price of pure potash is not appreciably higher than that of soda, potash only finds employment in enamel manufacture in special isolated cases—*e.g.*, for the production of American granite enamels on rough sheet iron, and for special ground and cover enamels (cryolite white).

Generally speaking, the substitution of potash for soda may be advisable for those enamels in which there is less desire for show (kitchen utensils) than for high lustre. For the same effect 100 kg. calcined soda may be replaced by 77 kg. of pure potash.

XV. SOME IMPORTANT ENAMELLING PIGMENTS.

Iron Oxide for Red Colours.—Iron oxide is found extensively in nature in large masses, and, under the names iron glance, red iron ore, and hæmatite, constitutes a valuable iron ore. Its chemical formula is Fe_2O_3, corresponding to 70 per cent. iron and 30 per cent. oxygen. Its specific gravity is 5·19 to 5·23.

To produce a red iron oxide for ceramic pigments, the starting point is not the mineral itself, but is from solutions of iron salts, for which a series of processes exist.* Pure iron oxide is obtained as a deep red amorphous powder by heating ferric hydroxide, $Fe(OH)_3$, or iron oxalate to redness, also by heating anhydrous iron vitriol (ferrous sulphate, $FeSO_4$), with common salt.

By strongly heating green vitriol and also ferric sulphate, $Fe_2(SO_4)_3$, red iron oxide is obtained, which still usually contains a slight sulphate content (Caput mortuum). The colour of the iron oxide can vary from a bright brick red through dark red to violet, according to the temperature and duration of heating. Great experience is, therefore, required in order to reproduce the same shades of iron oxide red. The concentration of the ferrous sulphate solution employed also plays a part.

The inexpensive iron oxide so obtained is only feebly fireproof, and requires a lower muffle temperature, since at higher temperatures the iron oxide forms a green-coloured ferrous silicate with the silica of the enamel.

For the preparation of a good red iron oxide, quite pure green vitriol is taken, finely pulverised, and gently warmed so that the crystals do not melt, but only evolve their water of crystallisation. This white anhydrous ferrous sulphate is again pulverised, and the finer this is performed the purer will be the colour; it is then placed in thin layers in a muffle, which is slowly raised to a red heat. As soon as the desired shade of red is attained (tested by allowing samples to cool), the heating is

* See Hermann's book, p. 36.

discontinued and the muffle allowed to cool slowly. The cold iron oxide is repeatedly washed with boiling water to extract any residue remaining of undecomposed iron sulphate, and then dried.

Another recipe reads :—17 parts of soda are dissolved in 68 parts of water, and the solution raised to the boil in an iron tank, 10 parts of crystallised green vitriol then being added with stirring. The greenish-white precipitate of ferrous carbonate, $FeCO_3$, formed is allowed to settle, filtered, washed, and allowed to oxidise in thin layers in the air until it is converted into yellow ferric hydroxide [$Fe(OH)_3$]. Afterwards the product is heated to redness, when, according to the time and temperature, different shades of iron oxide red are obtained.

An especially fiery red is acquired by Vogel's method, in which a saturated solution of oxalic acid ($C_2H_2O_4$) is poured into a boiling solution of ferrous sulphate, producing a greenish-yellow precipitate of ferrous oxalate (FeC_2O_4), which is collected, washed with water, and heated in a shallow iron dish to 200° C. Thereby the precipitate is transformed into a friable red powder of pure iron oxide.

The Colouring of Enamels by Red Iron Oxide.—Enamels coloured with iron oxide find extensive employment for the external enamelling of kitchen utensils. In the preparation of these enamels the red iron oxide is exclusively * added at the wet grinding of the enamel, and in quantities varying from 7 to 12 per cent., according to the quality of the oxide. The latter plays an all-important part in the production of beautiful red enamels, which should be stable during the firing. Many enamelling firms have often to contend with the difficulty that the red enamel easily assumes a poor brownish-red colour in the muffle, and, being less fire-proof, requires a firing temperature which is difficult to bring into unison with the melting point of the enamel. In such cases it is advisable to replace the iron oxide by a superior brand, and to make experiments with other conditions. Unfortunately, many manufacturers seek to work with as cheap red iron oxide as possible, to the disadvantage of their wares. Cheapness is hardly compatible with good quality, and, in addition, enamels coloured with badly heated and purified oxide exhibit sometimes the disagreeable appearance on their surface of an

* Occasionally cheap iron oxide or materials containing it are added to the raw mixture.

efflorescence of small white specks having a salty flavour. In such a case the iron oxide still contains ferrous sulphate, and must be excluded from use. A simple test to see whether iron oxide still contains sulphate is as follows :—In a test tube several grammes of iron oxide are boiled with water, the solution filtered, a drop of chemically-pure hydrochloric acid added, and then a few drops of barium chloride solution. The presence of minute traces of sulphate is revealed by a white turbidity, and often a white precipitate of barium sulphate.

Every enamel is not equally suitable for the preparation of red enamels. The latter should be especially free from saltpetre in the crude mixture.

Two suitable recipes for this purpose run as follows :—

Borax,	42 kg.	Borax,	60 kg.
Quartz,	91 ,,	Quartz,	34 ,,
Cryolite,	31 ,,	Felspar,	58 ,,
Soda,	6·3 ,,	Soda,	6 ,,
Clay,	3 ,,	Cryolite,	11 ,,
Magnesia,	2 ,,	Clay,	4 ,,
Fluorspar,	1 ,,		
Stannic oxide,	6 ,,		

At the mill 4 per cent. clay and 8 to 10 per cent. red iron oxide are added. On firing red enamelled wares an excessive temperature is always to be avoided. Also, setting agents must be avoided as far as possible for red enamels, and at the most only a few drops of water-glass solution (sodium silicate, Na_2SiO_3) should be added to the working dishes for the better adherence of the enamel to the utensil.

Chromium Oxide, chromic oxide, or chromium sesqui-oxide, Cr_2O_3, serves for the preparation of dark green enamels. It is prepared in various ways from chromium salt—*e.g.*, by heating potassium bichromate to redness with sulphur, extracting the mass with very dilute sulphuric acid, and washing the residue. The chromic acid is thereby reduced by the sulphur to chromium oxide. By treating the heated mass with sulphuric acid there are formed, in addition to chromium oxide, sulphur dioxide, potassium sulphide (K_2S), and a solution of potassium sulphate (K_2SO_4). The more sulphur employed, the brighter the shade of the green chromium oxide, and the purer the bichromate the more beautiful the colour. The presence of iron salts injures the colour. According to Her-

mann, 19 parts $K_2Cr_2O_7$ and 4 parts sulphur are employed, from which 9·33 parts of chromium oxide are obtained. According to A. Casali, 1 part of potassium bichromate is mixed with 3 parts burnt gypsum and strongly heated, the mass being afterwards boiled with very dilute hydrochloric acid. The chromium oxide is formed according to the following equation :—

$$2K_2Cr_2O_7 + 2CaSO_4 = 2Cr_2O_3 + 2K_2SO_4 + 2CaO + 3O_2.$$

The lime goes into solution on boiling with hydrochloric acid, and the residue is well washed with hot water and dried.

The potassium bichromate employed is previously finely-powdered and mixed with half its weight of powdered sulphur, then strongly heated in crucibles. The green spongy mass consists of chromium oxide and potassium sulphate, which latter requires care for its solution owing to its sparing solubility in water, although dilute acid favours its solution. The acid is thoroughly washed out, and the residue filtered and dried.

From 101 parts of potassium dichromate and 50 parts sulphur are obtained 68 parts of chromium oxide. Brongiart takes 1 part K_2CrO_4 (potassium chromate) and 2 parts sulphur. The chromium oxide formed must be thoroughly heated to redness after washing. Chromium oxide may also be obtained by heating ammonium chromate, $(NH_4)_2CrO_4$, and the lower the decomposition temperature the more beautiful the green after lixiviation and grinding.

In the wet way chromium oxide may be produced, although with a less fiery colouring power, when a solution of chrome-alum reacts with soda, whereby a greyish-green chromium oxide is formed, which, after washing and heating, gives pure chromium oxide.

If a solution of potassium bichromate be treated with hydrochloric acid and alcohol until no further action ensues, the liquid becomes an even darker green ; chromium chloride is produced, and by precipitation with soda solution furnishes chromium hydroxide. This colloidal precipitate, according to Brongiart, may be advantageously employed for the preparation of blue-green oxide, which latter is produced by mixing the still moist precipitate with moist cobalt oxide, drying, and strongly heating to redness. Very beautiful bright green shades are given by mixtures of non-ignited chromium oxide with oxide of antimony.

Chromium Oxide in Enamel Manufacture.*—Chromium sesquioxide finds manifold application in our industry for the preparation of green enamels. For this purpose the chromium oxide may be either fused with the raw mixture, or added in the form of a grinding addition at the wet mill. Usually 5 to 8 per cent. of the oxide is used. Fused enamel waste may also be advantageously used for the preparation of green enamels, since chromium oxide easily obliterates the colour of the enamel waste.

For example, the following mixture is fused in the tank furnace :—

200 kg. fused enamel waste,
20 kg. borax,
6 kg. soda,
12 kg. chromium oxide.

Enamels with chromium oxide exhibit now and then the disagreeable property that, after burning in the green enamel upon lamp shades, utensils, etc., the chromium oxide causes the latter to appear dull, while it may form a yellowish-coloured efflorescence on the surface of the enamelled ware. This phenomenon is connected with the quality of the imperfectly-produced chromium oxide, which may still contain undecomposed and unextracted potassium bichromate. A simple test suffices for investigating the purity of the chromium oxide—viz., a small sample is boiled with water and allowed to stand. If the clear supernatant solution is tinted yellow, trustworthy evidence is obtained of the incomplete character of the chromium oxide. In like manner the sparingly soluble potassium sulphate formed during the manufacture of chromium oxide may be the cause of enamel efflorescence. It is highly important, therefore, always to have the purest chromium oxide which has been thoroughly washed and submitted to prolonged red heat.

Pink Rosa (*Pink Colours, Nelkenfarben*).—The various shades of pink-red are among the most important of the cheap rose-colouring matters employed in ceramics.

The preparation of pink colours is brought about by heating to a frit mixtures of chalk, quartz, stannic oxide, borax, and potassium bichromate, extracting the pigment obtained with water (to remove the undecomposed excess of potassium chromate),

* See the latest valuable researches of Dr. G. Büttner and D. Berges, published in the *Sprechsaal*, Nos. 44 and 46 (1911), on the rôle of chromium oxide in glazes.

then levigating and washing.* These pink pigments have been known for a long time.

The recipes for their preparation are very numerous, corresponding to the possible colour shades, which may vary from a delicate-rose to a dark-rose violet.

One of these many recipes runs as follows :—

50 kg. stannic oxide,
25 kg. chalk,
18 kg. quartz,
4 kg. potassium bichromate,
6 kg. borax.

The constitution of the pink pigments is still uncertain, and recently two series of investigations by Petrik and Ross, on the one hand, and C. Purdy and H. Brown, on the other, have been made on this subject. While previously it was assumed that the red colour of pink pigments was due to a chromium stannate, L. Petrik† supposes that the phenomenon is due to chromium oxide distributed in extremely fine condition throughout the indifferent substance, stannic oxide. Petrik has produced red pigments in which aluminium was the basis, and lately he has made zinc glazes coloured red by chromium oxide.

The frit for this purpose had the following composition :—

$$2{\cdot}5\ ZnO,\ 0{\cdot}5\ K_2O\left\{\begin{matrix}3SiO_2\\3B_2O_3\end{matrix}\right\} + 4{\cdot}6 \text{ per cent. chromium oxide.}$$

The firing temperature was the Seger cone 8-10.

Even with zinc oxide alone there occurred a red pigment which was composed of approximately 66 parts chromium oxide and 34 parts zinc oxide. In this pigment the zinc is attacked only with difficulty. By the presence of alkaline earths (Ca, Ba) it is harder to obtain the red colour with certainty. A mixture suitable for this purpose is :—

67 parts bone ash,
200 parts dolomite,
50 parts Zettlitz kaolin,
116 parts quartz,
93 parts crystallised boric acid,
15 parts potassium bichromate.

* It is advantageous to wash with water which is weakly acid.

† *Sprechsaal*, 1907, p. 361. (Abstr. *Chem. Ztg.*, 1910, p. 524.)

Red chromium glazes occur when chromium oxide is added to an opaque or crystalline glaze. With tin glazes, which are the most opaque, the process meets with the greatest certainty, although tin is not absolutely necessary. If the conditions for devitrification have been favourably chosen, success may also be obtained with zinc and alumina glazes. The alumina-chromium oxide mixture gives a brilliant red pigment, and for this purpose 100 parts of commercial aluminium hydroxide are mixed with 6 parts of potassium bichromate and heated to redness with Seger cone 10-12, afterwards being well washed. The colour is a deeper red the more sharply it has been fired, and in the electric furnace it melts with a dark-red colour.

Ross, C. Purdy, and G. H. Brown (of Columbia, Ohio),* have likewise engaged in this work, the following commercial pink pigments serving as the basis of their experiments. The formulæ are calculated with stannic oxide as unity.

TABLE I.†

	CaO.	PbO.	KNaO.	SnO_2.	Cr_2O_3.	SiO_2.	
1	1·127	..	0·22	1·00	0·0218	0·437	Blood-red.
2	2·00	0·058	..	1·00	0·029	3·34	Bright red.
3	0·888	0·031	..	1·00	0·0155	1·00	Intense red.
4	0·744	..	0·062	1·00	0·0306	0·892	Brownish.
5	0·88	0·017	..	1·00	0·0086	0·922	Brick-red.
6	0·864	0·015	0·0844	1·00	0·115	0·970	Dark brick-red.
7	0·864	0·013	0·008	1·00	0·066	0·978	Pink.

From these formulæ the following principles may be deduced for the composition of new pigments :—

(1) All pigments should contain 1·0 equiv. of SnO_2 and 1·0 equiv. of SiO_2.

(2) The chromium and lime content may vary.

(3) Chromium is introduced as the green chromium oxide, or as lead chromate, or as potassium bichromate.

(4) The pigments must only be calcined, not fused.

(5) Further, they should not be washed after heating to redness.

* *Trans. Amer. Ceram. Soc.*, 1909, vol. xi., pp. 228-261. (Abstr. *Sprechsaal*, 1910, (21), pp. 308-309.)

† Taken from the *Sprechsaal*, 1910.

(6) The same glaze should be used throughout.

(7) In every case 0·1 equiv. of pigment—*i.e.*, 0·1 equiv. SnO_2—are added to the glaze.

Preparation of the Pigment.—Every pigment contains :—

1 equiv. SnO_2,
2 equiv. SiO_2,

and either 0·001 or 0·005 — 0·01 — 0·02 — 0·03 to 0·15 equiv. Cr_2O_3, and correspondingly 3·00 or 2·50 — 2·00 to 0·50 equiv. CaO, the chromium being added in the form of any of the above-named compounds. After an intimate mixing, the complex is fired in a crucible for thirteen hours in a Caulkins' gas muffle, the period being chosen so prolonged in order to attain a uniform distribution of heat and to adapt the experiments to technical conditions.

Preparation of Glazes.—The final glaze—*i.e.*, after the last additions—has the following composition :—

$$\left.\begin{matrix} 0{\cdot}22\ PbO \\ 0{\cdot}60\ CaO \\ 0{\cdot}18\ KNaO \end{matrix}\right\} \quad \left.\begin{matrix} 0{\cdot}16\ Al_2O_3 \\ 0{\cdot}1\ \ SnO_2 \\ x\ Cr_2O_3 \end{matrix}\right\} \quad \begin{matrix} 2{\cdot}1\ SiO_2 \\ 0{\cdot}475\ B_2O_3 \end{matrix}$$

The glaze proper consists of an unfritted and a fritted part. The latter contains :—

$$\left.\begin{matrix} 0{\cdot}625\ CaO \\ 0{\cdot}375\ KNaO \end{matrix}\right\} \quad 0{\cdot}23\ Al_2O_3 \quad \left\{\begin{matrix} 0{\cdot}72\ \ SiO_2 \\ 0{\cdot}989\ B_2O_3 \end{matrix}\right.$$

or

Chalk,	30·0 parts.
Borax,	38·2 ,,
Boric acid in flakes,	34·1 ,,
Felspar,	44·48 ,,
Kaolin,	7·77 ,,
Flint,	17·16 ,,

After pulverising and grinding the following were mixed with the frit :—

Frit,	0·48 equivalent.
Lead carbonate,*	0·22 ,,
Flint,	0·074 ,,
Clay,	0·05 ,,

* Further details are not given as to the chemical composition of the carbonate.

This glaze mixture formed the basis of every coloured glaze, and to it was also added :—

Pigment,	. . . .	0·1 equivalent.
Chalk,	. . . .	y „

The glazes were next coated on small prepared tiles and then fired at varying temperatures with an enveloping flame.

Three modes of firing were utilised :—

Up to Seger Cone 01.	Duration of heating	29 hours.	Fuel,	coke only.
„ 2.	„	„ 30 „	„	coke with a little coal.
„ 3.	„	„ 31 „	„	2 parts coke+1 part coal.

The furnace doors were opened at the end of the firing for cooling purposes ; during the process the heat was distributed as uniformly as possible.

The results, especially as regards the colour stages produced, were as follows :—

1. **Pigments**—*Group A* (with chromium oxide).—The mixtures with much lime (3·0 equiv. $CaCO_3$) gave no pink, with 2·5 equiv. a brownish shade, with 2·00, 1·5, and 1 equiv. $CaCO_3$ a pink-red, whereby the intensity increases with the chromium content. With 0·5 equiv. $CaCO_3$, the colour varies with growing chromium content from bright pink to dark green.

Group B (with lead chromate).—Here the colour changes vary much—*e.g.*, a part of the pigment with 3·0 equiv. $CaCO_3$ shows a pronounced pink—viz., that with 0·05 — 0·10 equiv. Cr_2O_3, while that poor in chromium possessed a bright yellow or green, and that rich in chromium a deep green. The pigment with 2·00 — 0·50 equiv. $CaCO_3$ was white to pink-red, the intensity increasing with the chromium content.

Group C (with potassium bichromate).— Here a partial volatilisation of green chromium compounds occurred after firing the pigment mixture, since green crystals were found on the edges of the crucible ; also the Seger cone exhibited a green tint in the muffle. The pigments with 3·00 equivs. $CaCO_3$ gave shades of bright green for those richest in chromium, varying to deep brown. With 2·00 — 1·00 equivs. pink prevailed, while at 0·50 equiv. the colour varied from lilac to bright green.

In general, group A appeared the most pink-red of similar commercial colours. The pinks of B were the lightest, while with C very characteristic brown colours were present. By

washing with water these pink varieties lost the brown colour and became a bright yellowish-brown, probably due to the presence of chromic acid on the surface. This is shown especially with pigments having 0·050 to 0·15 equivalent of Cr_2O_3. Here the point may be urged that the colour of the mixture is throughout no criterion for that of the glaze.

2. **Glazes.**—The group descriptions correspond to those of the pigments employed.

Group A.—Minute differences in the composition of glazes appeared to have no influence upon the firing temperature: moreover, all appear to be equally hard. With Seger cone 01 a single glaze here and there was defective, showing cracks and chipping, while in many glazes turbidity set in. With Seger cone 1-2 the glazes ran better, while the turbidity disappeared more and more. At Seger cone 3 the latter reappeared, the colour being already paler and not so deep as with Seger cones 01 and 1.

It may be again emphasized that the pigments should not be washed after heating, since the products are partially altered thereby in consequence of the soluble chromates being removed.

Results.—The authors establish that the nature of the union effected by the introduction of chromates into glazes has influence upon the colour produced, in contrast to the opinions of Seger, Rodgers, Mellor, and von Hull. Pigments of the same molecular composition, in which, however, the chromium has been introduced as different compounds, very seldom exhibit the same degree of colour.

Further, it follows from the investigations that with a high lime content 0·0001 equiv. suffices to produce a bright red in all three groups A to C. With decreasing lime content the shade in groups A and B becomes lilac, and in C a deeper red. The influence of the lime content on the colour is shown, especially in series B, with lead chromate, where a high lime content is accompanied by a deep red colour, which gradually fades as the amount of lime diminishes. In addition, this influence depends in general not only on the composition of the glaze, but also on that of the pigment. The former should be relatively poor in lead and alkali, and rich in lime.

The results of Purdy and Brown's work deviate considerably from some of those obtained by earlier ceramic investigators, especially with respect to the colour shades acquired, a circumstance to be traced either to the varying origin and purity of the

chromium oxide and lead chromate employed, or to the volatilisation of chromium compounds when potassium bichromate is heated to redness. As already mentioned, several pigments contain soluble chromates, which during cooling may become concentrated on the surface of the glaze layer. Both authors have expressed their intention of continuing this interesting study.

Brown and other pink colours may be likewise prepared by replacing stannic oxide with ferrous chromate or titanic oxide.

Pink Colours in Enamels.—The addition of these colours to enamel is made at the wet mill in quantities from 6 to 10 per cent., according to the quality of the colour and the shade desired.

This rose colour naturally cannot compete with the pink produced by gold salts as regards resistance to fire. Enamels coloured by pink-rose require a moderate firing temperature, otherwise the colour fades. The utensils to be coated with rose enamel must not be handled with perspiring hands before firing, as afterwards white spots may arise, due to the reduction of the pigment by the organic matter of the perspiration.

Yellow Pigments.—The following compounds serve for this purpose :—

(1) Acid potassium antimonate (falsely termed antimony oxide) in association with the oxides of zinc and iron. Metallic antimony is strongly heated to redness with 6 parts saltpetre ; the product is then ground and subsequently washed with cold water to remove the excess of saltpetre, the potassium biantimonate being filtered from the potassium antimonate which has passed into solution. The latter is converted into the former by bubbling carbon dioxide through the solution.

(2) *Naples Yellow.**—This yellow pigment, which found such extensive use in earlier times, is chemically lead antimonate, ($PbO + Sb_2O_5$). The quality of commercial Naples yellow is a varying one, and for its preparation tartar emetic 2 parts, lead nitrate 4 parts, and common salt 8 parts are mixed and melted together, the melt being then treated with very dilute hydrochloric acid, washed, and dried. According to the Paris method metallic antimony is oxidised by melting in presence of air 12 parts of antimony, 8 parts red lead, and 4 parts tin oxide, the mixture being fused at a gentle red heat.

(3) *Barium chromate* ($BaCrO_4$) is less often employed. Its

* According to Hermann's book, p. 25.

colour is a canary yellow, and for its preparation commercial barium chloride is dissolved in water and precipitated by the addition of potassium chromate solution, the precipitate being filtered and washed.

(4) *Lead chromate*, termed chrome yellow ($PbCrO_4$), generally contains lead sulphate or even gypsum as impurities, these being added for shading the colour. The latter is very fluctuating and uncertain. For its preparation a solution of lead acetate (sugar of lead) is acidified with acetic acid and a solution of potassium bichromate added so long as a precipitate forms. The precipitate is washed, and the beautiful dark-yellow product so obtained dried. For this purpose 100 parts of lead acetate solution and 40 parts of potassium bichromate solution are employed. In association with selenium the so-called coral-red is produced.

(5) *Cadmium Yellow or Cadmium Sulphide.*—In the endeavour to exclude from the enamel industry compounds containing lead, the beautiful yellow cadmium sulphide (CdS) has come into prominence. Only one form of it occurs in nature, known as "Greenockite."

It is prepared pure by passing sulphuretted hydrogen into a solution of a cadmium salt (cadmium chloride or sulphate). In dilute acids cadmium sulphide is insoluble.

For enamelling purposes the colouring power is great, and the addition of 1 per cent. suffices at the wet mill, although it may be fused with the raw mixture in the furnace. In the latter case an interesting observation may be made in that the molten yellow enamel so obtained, when cooled by running it from the tank or crucible furnace into cold water, assumes a white appearance, which turns to yellow again after grinding, covering, and firing the wares. This phenomenon is bound up with the physical conditions of rapid cooling, since thereby, as in the similar case of gold ruby glass, the cadmium sulphide remains dissolved in the enamel instead of separating out in a finely-divided condition, to appear again after the firing of the coated wares.

XVI. GENERAL ENAMEL RECIPES.

THE varying opinions entertained respecting enamel preparations are well illustrated by the following survey of molecular formulæ which have been published from time to time by different experts.

Vondracek gives* the following limiting values for ground enamels :—

$$\left.\begin{matrix}0{\cdot}5\text{-}0{\cdot}7\ Na_2O\\0{\cdot}2\text{-}0{\cdot}3\ K_2O\\0{\cdot}3\text{-}0{\cdot}0\ CaO\end{matrix}\right\}\ 0{\cdot}15\text{–}0{\cdot}35\ Al_2O_3\ \left\{\begin{matrix}0{\cdot}5\text{-}1{\cdot}1\ B_2O_3\\2{\cdot}0\text{-}3{\cdot}1\ SiO_2\\0{\cdot}0\text{-}0{\cdot}3\ F_2\end{matrix}\right.$$

and for a cover enamel on sheet iron :—

$$\left.\begin{matrix}0{\cdot}45\text{-}0{\cdot}7\ Na_2O\\0{\cdot}15\text{-}0{\cdot}3\ K_2O\\0{\cdot}4\ \text{-}0{\cdot}0\ CaO\end{matrix}\right\}\ 0\text{–}0{\cdot}55\ Al_2O_3\ \left\{\begin{matrix}0{\cdot}15\text{-}0{\cdot}7\ B_2O_3\\2{\cdot}0\ \text{-}4{\cdot}3\ SiO_2\\0{\cdot}0\ \text{-}0{\cdot}8\ F_2\\0{\cdot}3\ SnO_2\end{matrix}\right.$$

According to Shaw, the limiting values for a cover enamel are :—

$$\left.\begin{matrix}0{\cdot}0\text{-}0{\cdot}65\ Na_2O\\0{\cdot}0\text{-}0{\cdot}60\ K_2O\\0{\cdot}2\text{-}0{\cdot}60\ CaO\end{matrix}\right\}\ 0\text{–}0{\cdot}5\ Al_2O_3\ \left\{\begin{matrix}1{\cdot}0\text{-}1{\cdot}8\ SiO_2\\0{\cdot}2\text{-}\ ?\ B_2O_3\end{matrix}\right.$$

An anonymous author in the *Keramischen Rundschau*, 1908, pp. 98-100, 110-112, and 136-137, gives the following limits for ground enamels :—

$$\left.\begin{matrix}0{\cdot}54\text{-}0{\cdot}85\ Na_2O\\0{\cdot}27\text{-}0{\cdot}23\ K_2O\\0{\cdot}19\ CaO\end{matrix}\right\}\ 0{\cdot}31\ Al_2O_3\ \left\{\begin{matrix}2{\cdot}78\ SiO_2\\0{\cdot}75\text{-}0{\cdot}78\ B_2O_3\\0{\cdot}37\text{-}0{\cdot}38\ F_2\end{matrix}\right.$$

and for a cover enamel :—

$$\left.\begin{matrix}0{\cdot}41\text{-}0{\cdot}56\ Na_2O\\0{\cdot}29\text{-}0{\cdot}21\ K_2O\\0{\cdot}30\text{-}0{\cdot}23\ CaO\end{matrix}\right\}0{\cdot}35\text{–}0{\cdot}27\ Al_2O_3\left\{\begin{matrix}2{\cdot}54\text{-}1{\cdot}54\ SiO_2\\0{\cdot}27\text{-}0{\cdot}40\ B_2O_3\\1{\cdot}26\text{-}0{\cdot}88\ F_2\\0{\cdot}21\text{-}0{\cdot}37\ SnO_2\end{matrix}\right.$$

* *Sprechsaal Calendar*, 1910, p. 35.

Perhaps such limiting formulæ should only be regarded as of subordinate importance, since the experiments were performed either in the laboratory or on a relatively small scale. The practical man, however, knows that the properties of an enamel can only be established by large scale tests, and it is a question whether it were not more correct to deduce the relationship between the quantities of the separate compounds used (as the author has attempted to do) from a series of recipes tested in different works. Although a series of recipes in this chapter have been collected from the literature, the intention has been to provide the thoughtful practical man, desirous of experimenting, with a survey of the most important opinions respecting this subject. It is unnecessary, however, to emphasize the fact that all recipes from whatever source are not capable of universal application in the absence of specific detailed information.

American Pottery Enamels.—The following abstract is taken from an account in the *Sprechsaal*, 1910 (8), p. 108, of a comprehensive investigation by J. Bradfield Shaw (of Grand Rapids, Michigan), carried out in the State University of Ohio, and published in the *Transactions of the American Ceramic Society*, 1909, vol. xi., pp. 103-152. The work is certainly of great interest, although many of our European experts may be sceptical about it, especially with regard to the high fluorspar content of these American enamels, and also as to the views expressed concerning the rôle of lime.

Shaw's table, giving the composition of enamels in molecular equivalents, has been corrected by the author, to the better and more usual standpoint of percentage weights.

Shaw gives the following limits for ground enamels :—

$$\left.\begin{matrix} 0{\cdot}15\text{-}0{\cdot}75\ K_2O \\ 0{\cdot}0\ \ \text{-}0{\cdot}60\ Na_2O \\ 0{\cdot}14\text{-}0{\cdot}64\ CaO \\ 0{\cdot}0\ \ \text{-}0{\cdot}06\ CoO \\ —\ \ \ —\ \ MnO \end{matrix}\right\} 0{\cdot}1\text{–}0{\cdot}5\ Al_2O_3 \left\{\begin{matrix} 1{\cdot}1\text{-}1{\cdot}7\ SiO_2 \\ 0{\cdot}2\text{-}0{\cdot}5\ B_2O_3 \end{matrix}\right.$$

The art and experience of the expert consists in being able to work out enamel recipes, and adapt them to current local manufacturing conditions and raw material relationships.

In previous discussions, the enamel formula has been regarded from a molecular standpoint, though preference is now given to the above method.

Cover white for enamelled kitchen utensils :—

$$\left.\begin{matrix}0{\cdot}195\ K_2O\\0{\cdot}683\ Na_2O\\0{\cdot}122\ CaO\end{matrix}\right\}0{\cdot}34\ Al_2O_3\left\{\begin{matrix}0{\cdot}571\ B_2O_3\\2{\cdot}315\ SiO_2\\1{\cdot}390\ F_2\\0{\cdot}235\ SnO_2\end{matrix}\right.$$

Cover white on cast iron :—

$$\left.\begin{matrix}0{\cdot}19\ K_2O\\0{\cdot}80\ Na_2O\\0{\cdot}01\ MgO\end{matrix}\right\}0{\cdot}36\ Al_2O_3\left\{\begin{matrix}0{\cdot}42\ B_2O_3\\0{\cdot}516\ SiO_2\\0{\cdot}16\ SnO_2\\0{\cdot}99\ F_2\end{matrix}\right.$$

Lead-free powder enamel for cast iron :—

$$\left.\begin{matrix}0{\cdot}012\ MgO\\0{\cdot}156\ K_2O\\0{\cdot}832\ Na_2O\end{matrix}\right\}0{\cdot}273\ Al_2O_3\left\{\begin{matrix}1{\cdot}04\ SiO_2\\0{\cdot}572\ B_2O_3\\0{\cdot}322\ SnO_2\\0{\cdot}819\ F_2\end{matrix}\right.$$

In the following Table I., Shaw gives an empirical series, which has been thoroughly tested, while in Table II. the same data have been recalculated by the author for greater utility and comprehension.

SiO_2 (Experimental Series A).—A high silica content causes chipping of the enamel layer, while one too low promotes crack formation; also with rising silica content the enamel becomes more difficultly fusible. The allowable inferior limit is 1·1 equivalents as calculated from the above molecular formula. Enamels with higher silica contents possess a greater expansion coefficient than sheet steel, and therefore tend to chip, although better results are given at high-firing temperatures. The allowable maximum of 1·7 equivalents must, therefore, be rejected.

B_2O_3 (V. R. B.).—A high borax content promotes chipping, while one too low gives dull enamels, so that B_2O_3 has a fairly intense influence in each case. The allowable limits are 0·5 and 0·2 equivalents.

Al_2O_3 (V. R. C.).—This increases the brilliance and adhesive character of the enamel up to about 0·5 equivalent. At the same time, the enamel becomes more resistant towards fire, but also more viscous, so that it may be poured from the crucible in the molten condition only with difficulty. The allowable limits vary between 0·1 and 0·5 equivalent.

TABLE I.—Ground Enamels (from Shaw).

No. of the Experimental Series.	Felspar.	Flint.	Crystallised Borax.	Anhydrous Soda.	KNO_3.	Fluorspar.	Cryolite.	Cobalt Oxide, Co_2O_3.	Manganese Dioxide.	Chalk.	Clay.	$B_2O_3.3H_2O$.
A 4	0·1	0·57	0·19	0·22	0·06	0·24	0·06	0·006	0·004	..	..	..
A 5	0·1	0·77	0·19	0·22	0·06	0·24	0·06	0·006	0·004	..	..	..
A 6	0·1	0·97	0·19	0·22	0·06	0·24	0·06	0·006	0·004	..	..	..
B 3	0·1	0·77	0·09	0·32	0·06	0·24	0·05	0·006	0·004	..	..	..
B 6	0·1	0·77	0·24	0·17	0·06	0·24	0·05	0·006	0·004	..	..	..
C 2	0·1	0·77	0·19	0·22	0·06	0·24	0·056	0·006	0·004	..	..	..
C 5	0·1	0·77	0·19	0·22	0·06	0·24	0·056	0·006	0·004	..	..	..
D 2	0·1	0·77	0·19	0·22	0·06	0·24	0·05	0·006	0·004	..	..	..
D 7	0·1	0·77	0·19	0·17	0·06	0·24	0·05	0·006	0·004	..	..	..
E 2	0·1	0·77	0·19	0·32	0·06	0·14	0·05	0·006	0·004	..	..	..
E 7	0·1	0·70	..	0·10	0·02	0·64	0·02	0·006	0·004	..	0·03	0·18
F 2	0·1	0·77	0·19	0·22	0·06	0·24	0·05	0·006	0·004	..	..	..
G 3	0·08	0·90	0·19	0·388	0·082	0·24	0·08	0·006	0·004	..	..	..
H 1	0·1	0·77	0·19	0·22	0·06	0·24	0·05	0·006	0·004	..	..	..
H 5	0·1	0·77	0·19	0·22	0·06	..	0·05	0·006	0·004	0·24	..	..

TABLE II.—Ground Enamels.

No. of the Experimental Series.	Felspar.	Flint.	Crystallised Borax.	Calcined Soda.	KNO_3.	Fluorspar.	Cryolite.	Cobalt Oxide, Co_2O_3.	Manganese Dioxide.	Chalk.	Clay	Boric Acid.
A 4	24·8	15·2	32·2	10·4	2·8	8·3	5·6	0·45	0·15	..	..	..
A 5	23·5	19·6	30·6	9·8	2·6	7·9	5·3	0·43	0·15	..	..	..
A 6	22·5	23·0	29·2	9·4	2·4	7·6	5·1	0·40	0·14	..	..	..
B 3	26·8	22·3	17·0	16·3	2·9	9·0	5·1	0·48	0·17	..	..	..
B 6	22·4	18·6	36·8	7·3	2·4	7·5	4·2	0·40	0·14	..	..	..
C 2	23·6	19·6	30·7	9·9	2·6	7·9	4·9	0·42	0·15	..	..	..
C 5	28·2	4·2	36·5	11·8	3·1	9·4	5·9	0·50	0·16	..	..	..
D 2	23·7	19·6	30·8	9·9	2·6	7·9	4·5	0·71	0·15	..	..	..
D 7	23·4	19·4	30·4	7·5	2·5	7·8	4·4	0·42	0·15	..	..	..
E 2	23·5	19·5	30·5	14·3	2·5	4·6	4·4	0·42	0·15	..	..	..
E 7	28·4	21·4	..	5·4	1·0	25·4	2·1	0·51	0·18	..	..	..
F 2	23·8	19·7	30·8	9·9	2·6	7·9	4·5	0·42	0·15	..	3·93	11·4
G 3	17·3	21·0	28·0	15·9	3·2	7·2	6·5	0·39	0·14	..	..	..
H 5	23·6	19·6	30·6	9·8	2·6	..	4·4	0·42	0·15	8·6	..	..

Co_2O_3 (*V. R. D.*).—This increases the fire stability of the enamel, and renders it more readily applicable for melting purposes through a greater temperature interval than one without cobalt oxide. In addition, it strengthens the white colour of a white enamel over the ground layer of the mass employed. Although its addition to a ground mass is not absolutely necessary, yet it is eminently desirable. The addition limits, as given above, are mainly due to the high price of the oxide, and more than 0·06 equivalent is already too expensive for a cheap product.

CaO (*V. R. E.*).—An enamel containing no CaO, but only alkalies, is too soft for practical purposes. The lower limit is 0·14 CaO, and it is inadvisable to exceed 0·64 equivalent with corresponding reduction of the alkali content, since the enamel becomes fairly difficultly fusible.

Na_2O and *K_2O* (*V. R. F.*).—Both may replace each other at will without any noticeable effect. A high K_2O content, however, imparts a stronger lustre to the enamel.

Cryolite-Felspar (*V. R. C.*).—Replacement of felspar by cryolite causes the enamel to become appreciably softer and renders it opaque. High cryolite content and low felspar promotes crack formation, which probably depends on the volatilisation of a part of the silica as SiF_4. The best results were obtained when both components were added to the mixtures in equal amounts. At the same time, quartz must be added when cryolite replaces felspar, to maintain the SiO_2 content constant.

Chalk-Fluorspar (*V. R. H.*).—Here no difference may be detected in the action of either; the ware produced is of the same quality; in each case, A, the use of one or the other only depends on the local price.

These conclusions, derived from the experiments, are obviously only of value for the enamel formula, which has been taken above as the basis of the investigations. Since the distinction between the limiting values is so sharp on each side, important conclusions can be drawn in other respects with regard to the mutual relationships between the enamel components.

(2) **Cover Enamels.**—Shaw restricts himself here to white enamels, which are prepared exactly as ground enamels. They were coated upon the most trustworthy of the latter. An enamel

TABLE III.

No. of the Experimental Series.	Felspar.	Flint.	Borax.	Soda.	KNO_3.	Fluorspar.	Cryolite.	ZnO.	Sb_2O_3.	Crystallised Boric Acid	Clay Substance.	SnO_2.	Clay, Crude.
A 3	0·091	0·8	0·15	0·34	0·07	0·35	..	..	..	..	..	0·13	0·14
A 4	0·091	1·0	0·15	0·34	0·07	0·35	..	..	..	..	..	0·13	0·14
B 3	0·091	1·0	0·10	0·44	0·07	0·35	..	..	..	..	..	0·13	0·14
B 5	0·091	1·0	0·20	0·24	0·07	0·35	..	..	..	..	..	0·13	0·14
C 2	0·091	1·0	0·15	0·35	0·07	0·35	..	..	..	..	..	0·13	0·14
C 4	0·091	0·58	0·15	0·35	0·07	0·35	..	..	..	..	0·2	0·13	0·14
D 3	0·091	1·0	0·15	0·28	0·07	0·4	..	..	..	..	..	0·13	0·14
D 4	0·091	1·0	0·15	0·08	0·07	0·6	..	..	..	..	..	0·13	0·14
E 1	..	1·6	0·15	0·20	..	0·35	0·1	..	..	..	..	0·13	0·14
E 5	0·091	1·0	0·15	0·04	0·52	0·35	..	..	..	0·30	..	0·13	0·14
F 3	0·091	1·0	0·15	0·26	0·07	0·35	..	0·04	0·04	..	..	0·05	0·14

of the following composition served here as starting material for the investigation :—

$$\left.\begin{matrix} 0{\cdot}15\ K_2O \\ 0{\cdot}50\ Na_2O \\ 0{\cdot}35\ CaO \end{matrix}\right\} 0{\cdot}10\ Al_2O_3 \left\{\begin{matrix} 1{\cdot}60\ SiO_2 \\ 0{\cdot}30\ B_2O_3 \end{matrix}\right.$$

To this was added, after the first process, a further 10 per cent. SnO_2 and 2 per cent. clay. For the empirical composition, see Table II., No. A 4.

The empirical formulæ of the most trustworthy of the cover enamels in Table II. are given by the extreme members of the experimental series.

The results with respect to the influence of single compounds are as follows, the given limiting numbers referring to the equivalent formula without SnO_2 and clay :—

SiO_2 (A).—Increase of SiO_2 content makes the enamel harder, but also more acid resistant. The allowable limits are 1·0 to 1·8 equivalents.

B_2O_3 (B).—With increasing B_2O_3 content the enamel increases in lustre, but the melting point is depressed. The lower limit was 0·2 equivalent, but the upper was not attained.

Al_2O_3 (C).—This raises the opacity, lustre, and hardness of the enamel. Its presence is desirable, although not absolutely necessary. A content between 0 to 0·4 equivalent is recommended.

CaO (D).—This oxide acts most intensely upon the fusibility. If all the CaO be replaced by Na_2O, the glazes will be too soft for practical use. The CaO content should not be less than 0·2 equivalent.

K_2O and *Na_2O* (E).—These can be interchanged without any special effect. K_2O makes the enamels somewhat more brilliant than Na_2O.

Replacement of SnO_2 by *ZnO* and *Sb_2O_3* (F).—SnO_2 renders enamels opaque. It may be exchanged, wholly or partly, for ZnO and Sb_2O_3. 0·13 equiv. ZnO + Sb_2O_3, or SnO_2, suffices for the production of good covering layers, if a double cover be employed. The ZnO and Sb_2O_3 should be previously fritted before addition.

The firing temperature generally fluctuates between 870° and 925° C. This question, as well as the duration of heating, cannot receive further treatment here, since, as the author himself urges, the subject only possesses scanty data, and is therefore still

TABLE IV.—Cover Enamels. Recalculation of Table III. by Grünwald into Percentage Weights.

No. of the Experimental Series.	Felspar.	Flint.	Borax	Soda.	Fluorspar.	Cryolite	Zinc Oxide.	Antimony Oxide.	Crystallised Boric Acid.	Stannic Oxide.	Crude Clay.	Saltpetre.
A 3	20·3	19·2	23·0	14·4	10·8	..	..	..	..	7·8	1·5	2·8
A 4	19·3	22·9	21·8	13·7	10·4	..	..	..	..	7·4	1·3	2·7
B 3	19·9	23·7	18·2	18·4	10·8	..	..	..	..	7·7	1·4	2·7
B 5	18·8	22·3	28·2	9·4	10·1	..	..	..	..	7·2	1·3	2·6
C 2	16·0	19·1	18·1	11·8	8·6	..	..	..	..	6·2	17·5	2·2
C 4	17·4	12·0	19·6	12·8	9·4	..	..	..	..	6·6	19·1	2·4
D 3	19·5	23·2	22·0	11·4	12·0	..	..	..	..	7·5	1·4	2·7
D 4	19·9	23·7	22·5	3·3	18·5	..	..	..	..	7·3	1·4	2·8
E 1	..	39·0	23·1	8·7	11·1	8·5	..	..	..	7·9	1·4	..
E 5	16·1	19·2	18·2	1·3	8·7	..	..	..	11·9	6·2	1·1	16·8
F 3	19·7	23·4	22·2	10·8	10·6	..	1·3	4·5	..	3·9	1·5	2·8

a works' question, depending, moreover, on the degree of fineness, nature of the frit, thickness of the layer, etc. According to Shaw, it is not very difficult to obtain a good cover layer, if a trustworthy ground mass is already at hand.

Concluding Results.—The composition of ground enamels fluctuates between the following values :—

$$\left.\begin{array}{l} 0{\cdot}15 \text{ to } 0{\cdot}75\ K_2O \\ 0{\cdot}0 \text{ to } 0{\cdot}60\ Na_2O \\ 0{\cdot}14 \text{ to } 0{\cdot}64\ CaO \\ 0{\cdot}0 \text{ to } 0{\cdot}06\ CoO \\ — \text{ to } —\ MnO \end{array}\right\} 0{\cdot}1 \text{ to } 0{\cdot}5\ Al_2O_3 \left\{\begin{array}{l} 1{\cdot}1 \text{ to } 1{\cdot}7\ SiO_2 \\ 0{\cdot}2 \text{ to } 0{\cdot}5\ B_2O_3 \end{array}\right.$$

Similarly, the limits for cover enamels were :—

$$\left.\begin{array}{l} 0{\cdot}0 \text{ to } 0{\cdot}60\ K_2O \\ 0{\cdot}0 \text{ to } 0{\cdot}65\ Na_2O \\ 0{\cdot}2 \text{ to } 0{\cdot}60\ CaO \end{array}\right\} 0 \text{ to } 0{\cdot}5\ Al_2O_3 \left\{\begin{array}{l} 1{\cdot}0 \text{ to } 1{\cdot}8\ SiO_2 \\ 0{\cdot}2 \text{ to } ?\ B_2O_3 \end{array}\right.$$

Cast-Iron Enamels.—From *Sprechsaal*, 1909 (15), p. 220, by Vondracek. Eng. Pat. 2,539, A. D., 1856 (Salt).

	a.	*b.*	*c.*	*d.*	*e.*
Sand,	10	..	..	30	..
Flint,	..	36	..	..	6
Red lead,	33	..	..	45	..
Boric acid,	20	24	7	..	..
Glass fragments,	114	..	11	30	..
Soda,	16	24	0·25	4	3
Saltpetre,	1·15	18	..	4·5	2
Bone ash,	..	..	3·5	..	3
Arsenious acid,	..	..	..	3	..
Antimony oxide,	..	..	0·15	..	..
Pyrolusite,	0·60	..	..	..	..
Borax,	..	..	..	..	12

The cleaned cast iron is painted with gum, and the mixture "*a*" and "*b*" dusted on to it, the whole being heated until the coating melts, when a grey enamel coating results. In the case where a white enamel is required, the first coat is again painted with gum, one of the mixtures, *c*, *d*, or *e* dusted upon it, and then fired.

(2) Eng. Pat. No. 1,156, A. D., 1863 (Clark). 50 parts felspar, 30 quartz, 10 kaolin, 25 soda, 20 Spanish white, and 10

boric acid are fritted together, and then 60 parts of the frit are melted with 10 of felspar and 20 to 40 of white lead. 10 to 15 parts of the fused mass are ground, to which 1 to 10 parts of fat alumina clay are added. The enamel requires no ground mass.

(3) Eng. Pat. No. 12,554, A. D., 1906 (Atkinson and Smith). The enamel is prepared from 130 parts opaline glass fragments, 25 sodium bicarbonate, and 13 boric acid ; it requires no ground mass.

(4) Amer. Pat. No. 663,618 (Toping). The enamel is a melt of 61 parts borax, 71 felspar, 41 quartz, 15 fluorspar, 14 soda, 11 saltpetre, and a sufficient amount either of bone ash or other opaque or colouring agent. It may, if tin is absent, be coated direct on the metal.

(5*a*) D. R. P., No. 34,391 (Hörenz). This concerns a cover mass, consisting of 40 parts felspar, 28 borax, 8 tin oxide, 1 saltpetre, and 10 soda.

(5*b*) An enamel which may be directly coated on iron is prepared according to Eng. Pat. No. 9,611, A. D., 1893 (Leuchs) by the partial substitution of titanic acid for silica.

(6) D. R. P., No. 9,621 (Henzel and Broz). This deals with a series of enamels for cast-iron objects :—

(*a*)	28	parts	quartz,	11	soda,	6	chalk.
(*b*)	34	,,		11	,,	12	,,
(*c*)	34	,,		11	,,	12	,, 5 clay.
(*d*)	34	,,		6	,,	12	,,

(7) Eng. Pat., No. 15,129, A. D., 1899 (Zerzog), describes enamels which are easily rendered fluid, and which will cover objects, without requiring any ground mass, by a single dip into a molten bath. A readily fusible enamel may be prepared from 12 parts red lead, 4 borax, and 4 flint, or 12 parts red lead, 8 borax, and 3 flint.

A fireproof enamel is obtained from 12 parts red lead, 4 borax, and 5 flint, or 10 parts red lead, 6 borax, and 8 flint, with addition of 2 parts magnesia or 3 fluorspar.

A resistant enamel can be prepared from a mixture of 10 parts red lead, 6 sand, 5 borax, and 4 glass fragments.

(8) Enamels containing bismuth as a substitute for lead can be prepared according to Eng. Pat., No. 22,345, A. D., 1899

(Peyrusson), from 10 to 30 parts quartz, 10 to 60 boric acid or borax, 5 to 40 potash or saltpetre, 20 to 80 bismuth oxide, and 5 to 30 lithium compounds.

(9) A very simple glaze may be prepared according to Eng. Pat., No. 984, A. D., 1879 (Quinky and Baldwin), as follows :—One part borax and 1 part quartz are melted together, and the product poured into water. This is then ground with water, to which one-tenth of its weight of kaolin is added, and thickened by magnesium oxide or magnesium sulphate.

Cast-Iron Enamels.

Species of Enamel.	White.					Blue.	
Borax,	28	21	22·3	19	3	21	32
Boric acid,	..	..	..	..	14·40	..	..
Felspar,	40	46	46	32	26·08	46	24
Quartz,	..	..	..	..	13·04	..	16
Soda,	10	15	12	6·5	4·7	15	12
Saltpetre,	1	2	0·75	2·5	4·34	2	2·5
Cryolite,	..	..	..	1·5	11·04	..	2·5
Sodium silico-fluoride,	..	..	..	..	..	..	..
Stannic oxide,	8	10	15·5	8·5	..	..	4
Cobalt oxide,	..	..	..	..	..	1–2	2
Nickel oxide,	..	..	..	..	..	..	..
Pyrolusite,	..	..	..	..	..	..	..
Calcspar,	..	..	..	..	2	..	..
Red lead,	..	..	..	..	17·40	..	..
Magnesium carbonate,	..	..	..	..	2	..	..
Glass powder,	..	..	..	..	..	..	..
Fluorspar,	..	5	1	3	0·2	5	..
Clay,	..	..	..	..	..	..	..
Zinc oxide,	..	..	..	2·5	..	..	..
Bone ash,	..	..	..	1·5	..	..	..
According to	D. R. P. 34,291	Vondracek.			Eger.	Vondracek.	

PHYSICAL CONSTANTS FOR GLASS AND ENAMEL.

Specific Gravity of Enamels by Grünwald.

For cover white, including additions at the mill,				without water,	2·8
,,	,,	,,	,,	+ 30 % water,	1·8
,, ground enamel,	,,	,,	,,	without water,	2·04
,,	,,	,,	,,	+ 30 % water,	1·53

Coefficients of Cubic Expansion by Meyer and Havas.

(*Sprechsaal*, 1909, p. 497.)

Ground enamel,	$271{\cdot}45 \times 10^{-7}$.
Cover enamel,	$337{\cdot}35 \times 10^{-7}$.
Sheet iron for enamelling purposes,	$397{\cdot}06 \times 10^{-7}$.

Specific gravity of glass,*	2·2–6·3 grammes (Geolimeter system).
Tensile strength,	3·3–8·1 kg. per sq. cm.
Resistance,	60·6–126·4 kg. per sq. cm.
Elasticity,	4,800–7,970 kg. per sq. cm.
Specific heat,	0·08–0·23 gramme cal. ° C.
Thermal conductivity,	0·00108–0·00227 gramme cal. ° C. cm. sec.
Coefficient of cubical expansion (between 0°–100° C),	0·0000110–0·0000337 per ° C.
Average refractivity (D line),	1·465 –1·963 } Refractive index of air = 1.
Average dispersion (F and C lines),	0·00708–0·04882 }
Relative refraction,	19·7 –70 }
Dielectric constant,	5·5–9·1 for air = 1.

Table showing Enamel Consumption.

Thickness of the Sheet Iron in mm.	Percentage Enamel Consumption.	
	On Initial Weight.	On Final Weight.
0·10	128	56
0·20	64	39
0·30	43	30
0·35	37	27
0·40	32	24
0·50	26	20
0·60	21	17·6
0·70	18	15·5
0·80	16	14
0·90	14·3	12·5
1	12·5	11
2	6·4	6
3	4·3	4

* According to Dr. Zschimmer, *Die Glasindustrie in Jena*, p. 104.

Table of Initial Weights of Metal.

Sheet Thickness in mm.	1 Square Metre Sheet Iron weighs in kg.
0·10	0·78
0·20	1·56
0·30	2·34
0·35	2·73
0·40	3·12
0·50	3·90
0·60	4·68
0·70	5·46
0·80	6·24
0·90	7·02
1	7·8
2	15·6
3	23·4

Table showing the Increased Weight of Metallic Objects after their Primary Coating.*

Diameter of Roll in cm.	Thickness of the Sheet Metal in mm.	Surface in Square cm.	Net Weight in Grms. after Pickling.	Weight of Roll, in Grms., after its Primary Coating.	Consumption of Ground Enamel	
					Grammes.	Per cent.
20	0·25	628	52·25	62·35	10·1	18·3
20	0·30	628	63·25	73·35	10·1	15·3
20	0·35	628	74·25	84·35	10·1	13·1
20	0·40	628	85·25	95·35	10·1	11·5
20	0·45	628	96·25	106·35	10·1	10·2
20	0·50	628	107·25	117·35	10·1	9·2
20	0·55	628	118·25	128·35	10·1	9·3
20	0·60	628	129·25	139·35	10·1	7·6
20	0·65	628	140·25	150·35	10·1	7·1
20	0·70	628	151·25	161·35	10·1	6·5
20	0·75	628	162·25	172·25	10·1	6·1
20	0·80	628	173·25	183·35	10·1	5·7
20	0·85	628	184·25	194·35	10·1	5·4
20	0·90	628	195·25	205·35	10·1	5·1
20	0·95	628	206·25	216·35	10·1	4·8
20	1 mm.	628	217·25	227·35	10·1	4·6

* These tables are taken from the author's *Enamelling on Iron and Steel.* C. Griffin & Co., London, 1909.

Import and Export of Enamel Wares and Enamelling Raw Materials from Austria-Hungary in the Year 1909.

Official Statistics of the Austrian Minister of Trade.

Nature of Ware.	Import.		Export.		Remarks.
	Tons.	Value in Kronen.	Tons.	Value in Kronen.	
Fluorspar,	8,106	405,292	12	690	..
Aluminium,	411	741,060	143	279,630	..
Stannic oxide,	28	60,270	59	143,910	..
Hydrochloric acid,	897	41,290	3,263	150,107	..
Sulphuric acid,	27,233	1,634,004	10,938	601,585	..
Sheet enamel utensils,	61	91,050	422	320,948	Improbable.
Boric acid, crude,	34	10,140	..	..	..
,, Tuscan,	33	2	..	..	..
,, refined,	91	51,813	4	2,280	..
Borax,	139	52,668	3	1,400	..
Potassium saltpetre,	15	7,250	116	82,802	..
Soda nitre,	80,533	19,327,992	187	44,550	..
Potash,	189	70,309	5,668	1,550,717	..
Soda, crude,	148	8,146	523	36,026	..
,, calcined,	297	32,703	1,100	143,000	..
Felspar,	6,826	215,025	5,024	195,940	..
Natural cryolite,	555	343,852	..	..	..
Kaolin and clay,	56,351	1,548,931	354,980	11,246,945	..
Bituminous coal,	10,479,244	168,168,674	632,658	11,508,513	..
Coke,	701,281	17,623,526	197,313	6,004,261	..
Briquettes,	48,640	1,118,729	110,748	1,949,163	..
Lignite,	38,679	495,092	8,235,583	86,248,544	..
Fine Sheet Iron—					
Forged and dressed, 1·0–6 mm.,	121	31,959	38	7,980	..
Forged and dressed, 0·6–0·4 mm.,	523	141,102	5	1,103	..
Forged and dressed, below 0·4 mm.,	531	151,250	55	12,420	..
Black Sheet Metal—					
Below 1–0·6 mm.,	65	11,646	162	49,799	..
,, 0·6–0·4 mm.,	1,737	351,682	116	25,454	..
,, 0·4–0·15 mm.,	394	84,696	12	2,760	..

Mohs' Scale of Hardness.

1. Talc.
2. Gypsum.
3. Calcite.
4. Fluorite.
5. Apatite.
6. Orthoclase.
7. Quartz.
8. Topaz.
9. Sapphire.
10. Diamond.

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